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THE

PHYSICAL REVIEW.

THE IONIZATION OF POTASSIUM VAPOR BY LIGHT.

By R. C. Williamson.

Abstract.

Photo-ionization of potassium vapor by ultra-violet light to λ 1850 Å.—(1) *Jet method.* To insure that the light was not appreciably absorbed before it reached the vapor under observation, and to reduce thermionic and photo-electric emission to a minimum, a tube was used in which a jet of potassium vapor was directed from a heating chamber into the vacuum observation chamber (pressure about 10^{-4} mm.) and was there condensed on the walls, while a carefully diaphragmed beam from a quartz mercury arc was directed through the jet into a conical light trap. The presence of positive ions in the illuminated vapor was determined by means of the usual accelerating and retarding electric fields. (2) *Variation with wave-length.* By the use of a series of screens, the long wave-length limit for ionization was found to be between 2,800 and 3,100 Å., in agreement with the limit, 2,856 Å., calculated from the ionization potential by means of the quantum relation. No positive ions were obtained when the radiation was limited to wave-lengths greater than 3,100 Å. or when the jet was intercepted by a sliding shutter. As the wave-length was decreased below 2,800 Å., the ionization rapidly increased in amount; being apparently a continuous function of the wave-length. (3) *Variation with pressure* of the vapor in the jet was found to be linear. (4) *Proportion of exposed atoms ionized* was computed to be roughly 1 in 10^{10} for an exposure time of 10^{-5} seconds or 1 in 10^{5} per second for continuous exposure.

Photo-electric emission from potassium metal.—The electrodes, being coated with potassium, gave a photo-electric emission as a result of scattered light, which had to be corrected for in the measurements for the vapor jet. *The long wave-length limit* occurred quite consistently at 4,500 Å.; but there were indications of increased sensitivity below 3,000 Å. These results agree with the view that the limit is the same as for the vapor, provided the emissions observed for wave-lengths 3,000 to 4,500 Å. are due to impurities. A rough calculation indicates that the *proportion of exposed atoms ionized* was about the same as in the case of the vapor, for the same light intensity.

Series of ultra-violet absorption screens, transmitting to various short wave-length limits from 4,000 to 2,300 Å., including various solutions and glasses, are described and a spectrogram showing the transmission of each is reproduced.

EXPERIMENTAL results relative to the ionization of metallic vapors by light have been very meager,[1] and it is difficult to point to any

[1] Hughes, Bull. Nat. Res. Coun., 2, p. 86, 1921.

phenomena which are due, without doubt, to ionization by radiation of optical frequencies. Steubing[1] describes ionization of mercury vapor by light transmitted through fused quartz, but his results probably are to be explained as ionization in the vapor by collision of photoelectrons from the electrodes. Anderson[2] and Gilbreath[3] have published results obtained in potassium vapor which, however, can be accounted for by wall emission. Kunz and Williams,[4] in a brief abstract, state that while cæsium was not ionized by radiation of wave-lengths greater than 3130 Å., a marked effect was secured at 2,530 Å. No details as to the method seem to have been published.

In estimating the range of wave-lengths which must be used in order to secure ionization, a generalization of the quantum relation has been used by many writers. The equation $Ve = h\nu$, where V is the voltage corresponding to the energy of the electron, e the electronic charge, h the quantum constant, and ν the frequency of radiation, finds application in the field of x-rays, in calculating the maximum frequency of radiation excited in solids by electrons having energy corresponding to the voltage V. Or, conversely, it also can be used in computing the maximum energy of the secondary electrons liberated from solids by radiation of frequency ν.

Work in the metallic vapors indicates that in the case of the alkali metals the principal series of doublets is radiated when ionization of the vapor by electronic collision occurs, and the limiting frequency of the series is given by the substitution of the ionizing potential in the above equation. Conversely, when it is desired to ionize a vapor by radiation, thus liberating electrons, it is natural to assume that frequencies must be employed which are equal to, or greater than, the above limiting frequency calculated from the ionizing potential. The results of Kunz and Williams in cæsium vapor are at least in accordance with this view. In the case of potassium vapor, the observed ionization potential is 4.1 volts[5] and the corresponding series limit is 2,856 Å.[6]

The experiments here described were undertaken in an effort to secure definite evidence of the ionization of metallic vapors by radiation of optical frequencies and to investigate the ionizing power of the radiation as a function of the frequency.

Method.

In preliminary experiments it was found that glass and metals in the presence of potassium vapor at temperatures as low as 150° C. emit

[1] Phys. Zeit., 10, p. 787, 1909.
[2] Phys. Rev., 1, p. 233, 1913.
[3] Phys. Rev., 10, p. 166, 1917.
[4] Phys. Rev., 15, p. 550, 1920.
[5] Tate and Foote, Phil. Mag., 36, p. 64, 1918.
[6] Hughes, loc. cit., p. 168.

therm-electrons so freely as to mask any ionization currents produced in the vapor by light. Also such surfaces in the presence of potassium vapor, or when covered with solid potassium, may give a marked photo-electric emission if there is any scattered light. The procedure must then be determined so that currents consisting of positive ions due to radiation ionization can be distinguished from these electronic currents.

Absorption of the radiation by the vapor should be limited if possible to the region between the electrodes in order that active wave-lengths may not be absorbed before reaching the electric field.

Where accelerating fields are used, ionization by collision of electrons with the vapor may occur, and such an effect must be distinguished from ionization by radiation.

These considerations led to the adoption of the following method: A jet of potassium vapor *g*, Fig. 1*A*, was directed into a vacuum chamber

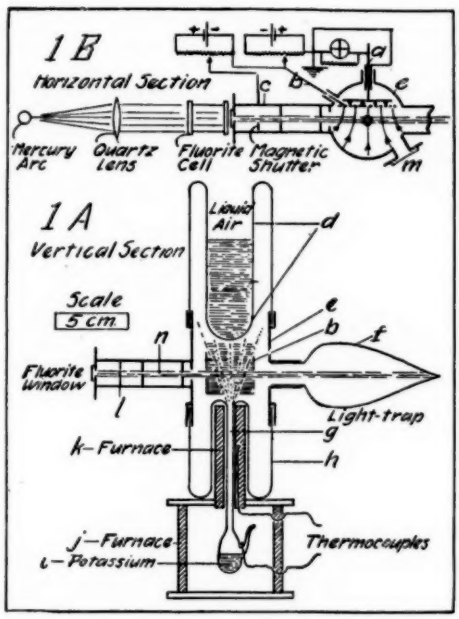

Fig. 1.

and condensed partly upon a glass surface *d*, cooled by means of liquid air, and partly upon the walls and electrodes of the chamber. A carefully diaphragmed pencil of light *n* traversed this jet a short distance from the nozzle and then entered a conical glass tube *f* serving as a light trap. A mercury arc in quartz was used as the source of radiation, and absorbing screens could be interposed between the arc and the vacuum

chamber. Electrodes were so arranged *a*, *b*, *c*, Fig. 1*B*, that the positive ions formed in the jet could be accelerated through a gauze, there to travel against a suitable retarding field to an electrode connected with an electrometer. Thus it will be seen that the radiation suffered no appreciable absorption till it reached the region between the electrodes, thermionic emission was limited to the parts of the nozzle, and the use of accelerating and retarding fields made it possible to distinguish positive ions from the electrons inevitably present.

Apparatus and Experimental Details.

The liquid air flask *d*, the light trap *f*, and the potassium reservoir and nozzle element *igh*, were all of glass fastened into the brass chamber by means of wax joints. The interior surfaces of the flask *d* and the jet element *h* (save in the tube *g* and reservoir *i*) were silvered and connected electrically to the brass chamber *e* for shielding purposes.

The potassium was distilled two or three times, the final operation carrying it into the reservoir *i*, the inlet tube then being sealed off. The reservoir *i* and the nozzle tube *g* could be heated independently, their temperatures being measured by means of thermocouples.

The sheet copper electrode *a* was provided with split insulation. The gauze electrode was of copper wire, No. 28, 20 to the inch. In both cases care was taken to provide flanges to protect the insulation from vapor scattered diffusely by the nozzle. The walls of the chamber itself served as the third electrode in most of the observations. The accelerating field V_a then was from the walls *ce* to the copper gauze *b*, and the retarding field V_r from the gauze *b* to the electrode *a*, Fig. 1*B*.

A magnetic shutter *l* was placed close to the fluorite window to protect it from scattered vapor while observations were not being made.

In one run, a sliding shutter (not shown in figure) placed over the nozzle of the jet made it possible to take readings with practically no vapor present, without waiting for the reservoir to cool down.

A side window of quartz *m* was provided as shown in Fig. 1*B*, so that the electrodes could be illuminated directly.

A Compton electrometer shunted with high resistances was used, the sensitivity in most cases being approximately 2,000 mm. per volt.

The arc was a Cooper-Hewitt quartz arc, running on about 73 volts and 4.0 amp.

A quartz lens, $F_{(5,890\text{Å}.)} = 7.9$ cm., was used with the arc at about the principal focus for 3,000 Å. to direct the light through the diaphragms.

Fig. 2 shows approximately the limits of the spectra transmitted by the absorbing screens, which gave a fairly regular series of steps from

Fig. 2.

R. C. WILLIAMSON.

4,500 Å. down to 2,360. The transmissions of the screens through the whole spectrum were not measured. Care must therefore be taken in interpreting the curves obtained with these screens, owing to gradual transition at the boundaries and possible absorptions of from 10 to 50 per cent. in the longer wave-lengths. As shown in the figure, the region from 4,500 to 3,100 Å. was covered by a set of glass screens which had been obtained from the Corning Glass Company. From 3,100 Å. down to 2,360, solutions in distilled water of phenol, phenyl-acetic acid, mercuric chloride, acetic and tartaric acids were used. The figures in parentheses following the substances, Fig. 2, give the number of parts of solution to 1 part of an approximately saturated solution of the substance. The cell was fitted with fluorite windows, the thickness of the fluid layer being 3.2 cm. Suggestions as to proper solutes for this work were due to Mr. Dahm of this laboratory, who will shortly publish more detailed results as to screens for this region.

A liquid air trap was placed between the diffusion pump and the ionization chamber. The pressure during most of the observations was less than 10^{-5} mm. at the gauge. However, since there was a slight leak and some evolution of gas from the different parts, it may have been as high as 10^{-4} mm. in the chamber.

Some trouble was experienced due to unsteadiness of readings at times, the cause of which was uncertain. Thermostats were not used on the furnaces, the heating currents being varied as indicated by the observed thermocouple reading.

It was necessary to work as rapidly as possible at the high temperature used, because the potassium soon distilled out of the reservoir, and the apparatus had to be taken completely apart and cleaned. Therefore no more points were taken on curves than was considered necessary to bring out the main features.

Results Showing Photo-ionization of Potassium Vapor.

Curves *ghi* and *g'h'i'*, Fig. 3*a*, are typical. The former was obtained as follows: Holding the retarding potential constant at 5 volts, the accelerating field was varied and the currents to the electrometer plotted versus the applied accelerating voltages, when the jet was traversed by the beam of unscreened radiation. The terms "accelerating" and "retarding" are used throughout the paper with reference to positive ions. This procedure was then repeated with screen No. 9 interposed, which cut out somewhat gradually wave-lengths less than 3,100 Å., giving the curve *g'h'i'*. Pairs of such curves were obtained for retarding potentials of 1, 5, 10, and 20 volts, as shown by the curves lettered *abc*, *ghi*, *jkl*,

and *mno*, respectively, together with the corresponding dotted curves with primed lettering. The data for the 20-volt curves was taken in a different run from the others, with a slightly different arrangement of parts on the interior of the chamber.

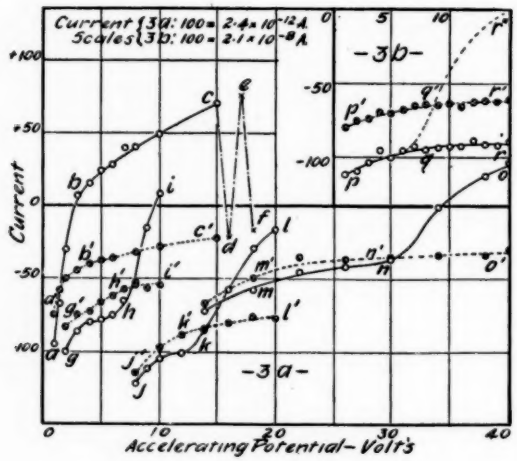

Fig. 3.

Considering the curve *ghi*, we see that beginning at about 2 volts there is a negative current *gh*, which decreases in magnitude, at first rapidly, then slowly, and then shows a decided bend upward *hi* just above 5 volts. The portion *gh* is due to photoelectrons from the gauze which are carried to the electrode *a* by the retarding field, together with some thermions from the nozzle of the jet, and the decrease is due to diversion of some of this current by the accelerating field. The upward bend *hi* is due to the superposition of the positive ions which are driven by the accelerating field through the retarding field to the electrode *a*. If the curve *ghi* were continued to higher voltages, it would turn toward the right again, approaching saturation, as shown in the corresponding part *bc* of the curve *abcε*, where the initial portion corresponding to *gh* does not occur, owing to the low voltages.

The potential at which the inflection due to the positive ions appears is not equal to the retarding potential, since these ions start from a point intermediate between the electrodes, and the energy which they acquire in the accelerating field is equal to some fraction of the applied accelerating potential V_a. By extrapolating the portions of maximum slope of the parts *hi*, *kl*, and *no*, to intersect with the continuations of the portions *gh*, *jk*, and *mn* respectively, this fraction is seen to be approximately 2/3 for the greater number of the positive ions.

When the beam of radiation is screened, the negative current gh is reduced in magnitude to $g'h'$, because of intensity loss in the beam both by reflection and by the screening out of the region below 3,100 Å. The inflection, however, showing the presence of positive ions has disappeared, and there is no indication of ionization comparable in magnitude with that observed without the screen.

These positive ions are not due to ionization by collision of photo-electrons from the gauze, for the following reasons.

In the case of curves taken at low potentials, it might be true that the interposition of the screen would reduce the initial energy of the photo-electrons from the gauze to such an extent that the energy gained in the accelerating field would not be sufficient to produce ionization, thus producing the difference observed in the screened and unscreened curves. However, even if we suppose that the screen reduces the emission energy of the gauze electrons to zero, the dotted curves should show an inflection as soon as the accelerating potential V_a becomes greater than 3/2 of the ionizing potential, and also greater than the retarding potential V_r. As a matter of fact, also, the majority of the photoelectrons have very low initial energies, so that the curve *abc* should not show strong ionization until $V_a > 6.2$ volts $> V_r$, whereas it approaches saturation at about 3 volts. The inflection due to the positive ions thus depends upon the retarding and not upon the accelerating potential. Slight inflections were observed in some of the screened curves (not published) which occurred around 5 volts, which would correspond approximately to ionization by collision, but they were too small for any definite conclusions to be drawn.

A further test of the above question was made by illuminating the gauze directly so as to make its photo-electric emission of a larger order of magnitude than the emission in the previous observations. The results are shown in Fig. 3*b*. The negative currents here were of the order of 10^{-8} amp. as compared with 10^{-12} amp. in the previous measurements. Curves were taken as before with and without a screen, at a retarding potential of 5 volts. The unscreened curve *pqr* in this case shows no noticeable indication of positive ions formed by collisiom, which would cause a deflection about as shown by the dotted portion qr''.

The above curves, then, are considered as conclusive evidence that the ionization of potassium vapor by means of radiation of wave-lengths between about 3,100 Å. and 1,850 Å. (the latter being taken as the approximate lower limit of the quartz arc spectrum) has been obtained.

Scattering of Light by Vapor.

In one run as shown at the end of curve *abc*, Fig. 3*a*, the jet was interrupted by means of the sliding shutter over the nozzle. The current then dropped from *c* to *d*. That is, the positive current disappeared, leaving the negative photoelectric current from the gauze. When the shutter was withdrawn, the current rose to the value at *e*, approximately the same as at *c*. Then the screen was inserted and the current again dropped to *f*, showing that the effect of putting in the screen was about the same as that of stopping the jet. This indicates that radiation scattered by the vapor is not an appreciable factor in producing the photo-electric emission from the gauze, and that most of the scattered light is from the diaphragms and the trap. In this connection, it might be noted that if there was fluorescence in the vapor jet, it was not strong enough to be visible. However, conditions were not particularly favorable for the detection of faint fluorescence.

Ionization as a Function of Wave-length.

The series of filters was then used to investigate the ionizing power of the different portions of the arc spectrum. With the retarding potential set at 1.2 volts and the accelerating potential at 10 volts, readings were taken as the screens were successively inserted in the path of the light, giving the curve *cde* in Fig. 4. The curve *cfg* was taken later, when the

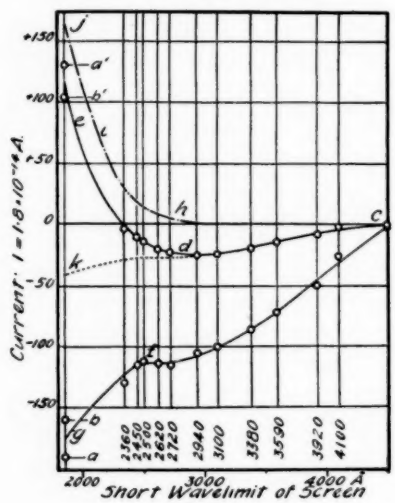

Fig. 4.

potassium in the reservoir was at room temperature, no vapor being present, thus giving the effect of the screens upon the photo-electric current

from the potassium-covered surfaces due to scattered light. The current scale does not apply to this curve. The points *a* and *a'* were taken with the radiation unscreened; *b* and *b'* were taken with the empty fluorite cell inserted. The mean of the two was taken as an approximate correction for reflection at the surfaces of the screens. Using this curve, a rough extrapolation of the branch *cd* can be made as shown in the dotted portion *dk*. The ordinates then between *dk* and *de* are a measure of the positive current and are plotted in the broken curve *hij*. This current starts in the vicinity of 2,900 Å. and increases very rapidly as the wave-length decreases. The energy contained in the arc spectrum between 1,850 and 2,360 Å. is probably about equal to that between 2,360 and 2,500, while it is less than 2 per cent. of that between 4,100 and 4,500 Å., according to estimates made from mercury arc energy distribution curves given by Suhrman.[1] Therefore the ionization per unit incident energy seems to be increasing very rapidly as the wave-length decreases. The form of the curve between 1,850 and 2,360 Å. is conjectural, and there is no information as to where a possible maximum would occur. The wave-length at which the positive current begins is somewhat uncertain owing to the characteristics of the screens. Three curves were taken, two at different times with one set-up, and the third with a slightly different internal arrangement, and in all three the positive current sets in between 2,800 and 3,100 Å. This agrees, within the limits of experimental error, with the calculation from the ionizing potential, using the quantum relation, which gives 2,856 Å. as the critical wave-length.

This ionization of the vapor by radiation does not seem to be associated with a resonance phenomenon, such as the absorption of a single wave-length in the vicinity of 2,856 Å. Rather, it appears to be a continuous function of the wave-length, starting near the convergence wave-length of the principal series and increasing quite rapidly as the wave-length decreases, giving a continuous absorption of energy below this limit. It is of interest to note in this connection the region of continuous absorption described by Wood[2] in the case of sodium vapor, which extends from the convergence wave-length of the principal series on down in the ultra-violet, thus corresponding with the region of ionization and probable consequent absorption observed for potassium.

Ionization as a Function of Pressure.

An attempt was made to obtain the current due to the positive ions as a function of the pressure in the reservoir. With the accelerating

[1] Ann. d. Phys., 67, p. 79, 22.

[2] Phil. Mag., 18, p. 531, 1909.

and retarding potentials set at 10 and 1 volts respectively, readings were taken with and without screen No. 9, as the reservoir cooled down. At low temperatures, the ionization current is very small compared with the additive negative current correction. This probably accounts for the variation of values for the two runs at low pressures, and the intercepts obtained. The results are shown in Fig. 5. The data for the

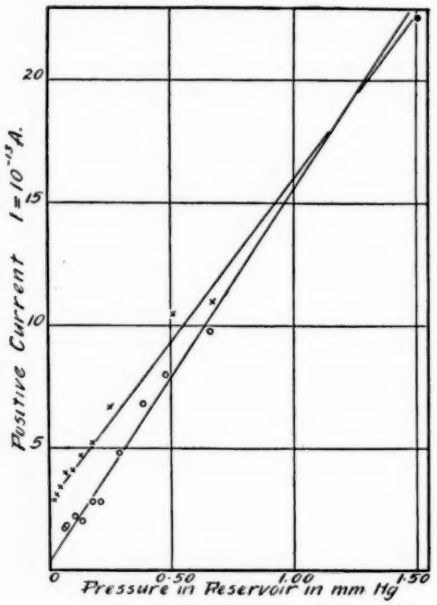

Fig. 5.

saturated vapor pressures of potassium were taken from a paper by Kroner.[1] The point at 1.5 mm. was taken between the two runs and was used in plotting both curves. The temperatures of the reservoir ranged from 225 to 356° C.

Photo-electric Current from Solid as a Function of Wave-length.

Referring to curve *cfg*, Fig. 4, it is seen that the long wave limit under the conditions of these experiments was about 4,500 Å. as compared with about 5,500 Å. which has been obtained in some previous work by Souder [2] and Pohl and Pringsheim [3]. As Hughes [4] states, results are very conflicting as to the long wave limit for solids, and the above seems to be further

[1] Ann. d. Phys., 40, p. 447, 1913.
[2] Phys. Rev., 8, p. 318, 1916.
[3] Verhand. d. Deut. Phys. Ges., 8, p. 357, 1910.
[4] Loc. cit., p. 102.

evidence to that effect. In several curves taken during these experiments, the limit occurs quite consistently at 4,500 Å. Some of the curves were taken while the jet was active and fresh potassium depositing, and others taken some hours after the jet had ceased, the surfaces standing in the vacuum. However, the vacuum conditions were not of the best, and the pressure was probably at no time lower than about 10^{-4}mm.

There is a rather interesting possibility suggested by the curve *cfg*, Fig. 4. In the absence of accurate data as to the transmissions of the screens throughout the whole range of wave-lengths, the curves may be interpreted in two ways. According to one viewpoint, the wave-length sensitivity of the solid is of the same order of magnitude from about 4,000 Å. down to 2,500, where a minimum occurs, followed by a very rapid rise *fg*. This increase of sensitivity of the solid may correspond to the ionization of the vapor, though it is shifted to somewhat shorter wave-lengths according to the curve. Hallwachs[1] considers that for pure metals the long wave limit should be the same in the solid state as in the vapor, and that currents observed for longer wave-lengths are due to modification of the photo-electric properties of the metal by impurities. Thus the current above 2,900 Å. in this case would be due to impurities present when the potassium was deposited in the vacuum chamber, while the current below 2,900 would represent that due to the pure metal. However, it is quite possible that this increase in current *fg* is due to variation with concentration of the general absorption of the screens throughout the longer wave-lengths. Thus the rise at 2,360 and 2,450 Å. would be due not so much to the additional energy below these limits as to that in the region up to 4,500.

Relative Photo-electric Sensitivity of Vapor and Solid.

The term "sensitivity" is here used to apply to total emission throughout the solid, rather than to the electrons escaping from the surface. Using results from the above experiments, an estimate can be made as to the order of magnitude of the number of atoms exposed for a second to a given intensity of radiation, for each electron ejected, in the vapor state as compared with that for the solid. Certain assumptions are involved which will be stated. For the vapor calculations, current data is obtained from curve *hij*, Fig. 4, for the region from 2,500 to 1,850 Å. In the case of the solid, it will be of interest to consider two regions of wave-length, that from 3,920 to 3,590 Å. (max. sensitivity in longer wave-lengths), and also from 2,500 to 1,850 Å.. corresponding to the region

[1] Phys. Zeit., 21, p. 565, 20.

chosen for the vapor. The current data for the solid calculations are taken from curve *pqr*, Fig. 3*b*, together with curve *cfg*, Fig. 4, from which the current distribution with wave-length is taken.

Case 1 — Vapor.

Data:

Wave-length 2,500 to 1,850 Å.
Mass potassium evaporated = 5 g.
Time = 19,800 sec.
Average temp. reservoir = 325° C.
Average vapor pressure in reservoir = 0.7 mm.
Cross section at nozzle of jet = 0.28 sq. cm.
Length of jet tube = 22 cm.
Cross section of pencil of light = 0.20 sq. cm.
Distance nozzle to light pencil = 2 cm.
Current = 3×10^{-12} amp.

Assumptions:

Velocity of discharge equals thermal velocity corresponding to temperature of reservoir.

Limiting cases were determined by assuming:
cylindrical vapor jet distribution, or
cosine distribution as in effusion, where free path is comparatively large;
cylindrical pencil of light, or
rough estimate of actual distribution.

Number of ions formed is proportional to the time of exposure. The time of exposure of each molecule in the jet being about 10^{-5} sec., reduction to 1 sec. exposure is made on basis of porportionality.

Current reaching receiving electrode represents total current, neglecting grid loss and incomplete saturation. This may involve a factor of two or three.

On the above basis, in the case of the vapor, it is calculated that the number of molecules N exposed to the given intensity of radiation for one second, for each ion formed, was between 10^5 (effusion distribution) and 2×10^6 (cylindrical distribution). 10^5 is considered to be more nearly correct for the following reasons: The density at the mouth of the jet was calculated from the mass discharged and the time of discharge as 1.6×10^{-8} g. per c.c. The density in the reservoir, from the vapor pressure, was 0.7×10^{-6} g. per c.c. Hence the free path at the nozzle is comparatively large, being about 1 cm., using argon as a basis. In support of the low pressure obtained at the nozzle may be mentioned

a check calculation as to the rate of discharge, using an empirical formula by Knudsen.[1] Substitution of a negligible pressure at the nozzle, and 0.7 mm. in the reservoir, gives about 4 g., which is in good agreement with about 5 g. observed.

Case 2—Solid.

Data: (Notation given below)

Wave-length 3,920 to 3,590 Å.
Current = 3×10^{-9} amp. per sq. cm.
$\alpha = 0.17 \times 10^{6}$.
$\gamma = 3.75 \times 10^{6}$ cm.$^{-1}$.
$I_0 = 3I$.

Assumptions:

Photoelectrons produced on the interior which do not emerge can be allowed for by using a method of analysis somewhat similar to that of Compton and Ross.[2] On this basis it is found that

$$n_1 = \frac{\nu I_0}{2}\left[\frac{\gamma}{\alpha^2}\log\frac{\gamma}{\gamma+\alpha}+\frac{1}{\alpha}\right],$$

where

n_1 = no. electrons emergent per sq. cm.
ν = no. of photoelectrons per unit intensity of radiation per cu. cm.
I_0 = intensity of light just inside surface of metal.
I = incident intensity.
$1/\gamma$ = mean free path of electron in metal.
α = coefficient of absorption of light in metal.

Where α is small relative to γ as in the present case, a sufficiently close approximation is obtained upon taking the limit as α approaches zero of the above expression. In which case

$$n_1 = \frac{\nu I_0}{4\gamma}$$

and

$$N = \frac{\text{No. of atoms per cu. cm.}}{\nu I}.$$

γ for platinum is used, since the value for potassium is not known. The two are probably of the same order of magnitude, the free path in potassium possibly being two or three times that for platinum.

α was obtained by extrapolation, using optical constants given by

[1] Ann. d. Phys., 28, p. 78, 1909.
[2] PHYS. REV., 13, p. 376, 1919.

Duncan.[1] It seems safe to assume a decrease in α for wave-lengths as low as 1,850 Å., in view of the transparency of the homogeneous films obtained by Wood[2] at low temperatures.

The intensity I is assumed to be the same as for the vapor, since the arrangement of the arc and lens was practically the same as in the case of the vapor observations.

The area illuminated was assumed to be of the order of magnitude of 1 sq. cm. This is very approximate, since a gauze was used, which was illuminated directly and by reflection on the reverse side.

The relation $I_0 = 3I$ was obtained by estimating the energy in the radiation from 3,920 to 3,590 Å. as compared with that for 2,500 to 1,850 Å. from the curves of Suhrman, and correcting for reflection by means of data from paper by Miss Frehafer.[3]

Calculations based upon the above data and assumptions give the number of atoms exposed for a second to the radiation I, per electron ejected, as 1.4×10^5.

A similar calculation for the region from 2,500 to 1,850 Å., where

$$\text{Current} = 7 \times 10^{-9} \text{ amp. per sq. cm.},$$
$$\alpha < 0.17 \times 10^6,$$
$$I_0 = I,$$

gives $N = 2 \times 10^4$, which is of the same order of magnitude as for the longer wave-lengths.

Comparing these figures with that for the vapor, we see that they are of the same order of magnitude, and that about one in 10^5 atoms exposed to the intensity of radiation used in the above experiments was ionized per second, whether in the vapor or in the solid state. It seems useless to speculate further in this matter until more accurate results have been obtained. The investigation is being continued.

Summary.

The foregoing results can be summarized as follows:

(1) It is believed that conclusive evidence of ionization of potassium vapor by ultraviolet light has been obtained.

(2) This ionization begins with wave-lengths of about 3000 Å., and increases rapidly and continuously in amount as the wave-length of the exciting radiation decreases from 3,000 to 1,850 Å., the limits investigated.

(3) The wave-length at which the ionization appears is in agreement,

[1] Phys. Rev., 1, p. 294, 1913.
[2] Phil. Mag., 38, p. 99, 1919.
[3] Phys. Rev., 15, p. 117, 1920.

within limits of accuracy of experiments, with that calculated from the ionization potential by means of the relation $Ve = h\nu$.

(4) The long wave limit of the photo-electric emission from solid potassium, obtained under the conditions of these experiments, was about 4,500 Å., as compared with about 5,500 Å., obtained by other observers.

(5) There was indication of a rapid increase in the photo-electric emission from solid potassium, beginning slightly below the wave-length at which the ionization of the vapor begins. This may be interpreted in accordance with the view that the long wave limit for pure potassium in the solid state is the same as for the vapor, and that the emission observed at longer wave-lengths is due to the action of impurities.

(6) Calculations were made which furnish evidence that the number of atoms exposed for a second to a given intensity of radiation, per electron ejected from an atom, is of the same order of magnitude in the solid as in the vapor state, for wave-length regions corresponding to marked sensitivities in each case. For the intensities used in these experiments, this number was about 10^5.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
August 26, 1922.

SECONDARY ELECTRON EMISSION FROM COPPER AND COPPER OXIDE SURFACES.

By Lawrence E. McAllister.

Abstract.

Secondary electron emission from copper and copper oxide.—A four-electrode tube of cylindrical symmetry was used in which electrons from a central equipotential Wehnelt cathode could be accelerated through holes in two grids, bombard the outer cylinder, the "plate," and cause the emission of secondary electrons which would either return to the plate or go to the grid according to the relative potentials. From the ratio of the plate currents when all and when none of the secondaries returned, *the number of secondaries per primary electron* was determined for pure copper and found to increase rapidly with the energy of impact at first but less and less rapidly as the accelerating voltage was increased, reaching the values 0.65 and 1.25 for 100 and 750 volts respectively. The surface of the copper plate directly opposite the holes in the grid gradually became blackened due to the formation of oxide, and as this layer of oxide increased in thickness the relative number of secondaries increased, whereas when the layer was reduced with hydrogen the relative number decreased toward the value for pure copper. *Variation with temperature.* By means of an auxiliary heating coil the plate was heated up to 450° C., care being taken to prevent leakage through the heated insulation, but the relative number of secondaries was found to be independent of the temperature. Some evidence was obtained of the presence of a small number of *high speed secondaries*, reflected or re-emitted with speeds comparable with that of the primary electrons.

Ionization potential of copper and copper oxide, as indicated by the current-voltage curves, is higher for the oxide than for copper, increasing with the thickness of the oxide layer from about 6 to over 10 volts.

Introduction.

THIS is a report of further work on experiments already published by Millikan and Barber[1] and by Barber[2] in 1921. The apparatus used is the same as that described by Dr. Barber[3] except for a few changes in electrical connections outside of the tube itself. These connections are shown diagrammatically in Fig. 1.

The essential parts of the four electrode-tube are in brief as follows:

1. The source of electrons is an equipotential electrode consisting of a platinum cylinder, 3 mm. in diameter, coated with the oxides of barium and calcium and heated indirectly by a central tungsten wire, insulated from it by a layer of alundum cement. The emitter is connected at one end with the wire carrying the heating current.

[1] National Academy of Science, Vol. 7, No. 1, page 13, Jan., 1921.
[2] Physical Review, Vol. XVII., page 322, 1921.
[3] Figure 2, page 326, Physical Review, Vol. XVII., 1921.

2. Concentric with the filament is a copper cylinder, *s*, 1.8 cm. in diameter, which will be called the grid No. 1, or the shield, because its purpose is to shield the second cylinder from the primary electron stream. About one fiftieth part of its surface is perforated with holes uniformly placed 1 mm. in diameter.

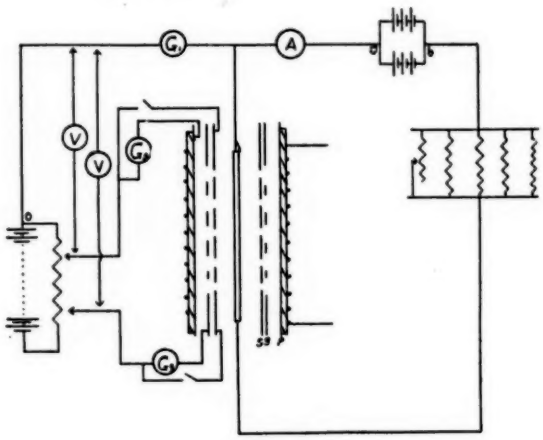

Fig. 1.

3. Just outside of the shield is another copper cylinder, *g*, 2 cm. in diameter, concentric with it and insulated from it by two porcelain rings. Call this the grid No. 2 or simply the grid. It is also perforated with holes, 3 mm. in diameter and in line with the holes of the shield.

4. Concentric with these two cylinders is a third, of copper, 3 cm. in diameter, which is called the plate. The inside surface of the plate is the surface to be studied.

5. The plate can be heated by a coil of nichrome wire wrapped around it and insulated from it by a soap-stone cylinder 2 mm. thick.

6. All cylinders are sealed in a pyrex glass tube and are supported by tungsten leads.

7. The vacuum system is capable of producing 5×10^{-6} cm. mercury pressure, and the observations were made at pressures of that order of magnitude.

The most important changes in apparatus are:

1. The introduction of a galvanometer, G_1, in the filament circuit to control the source of electrons, instead of using the ammeter A alone.

2. The use of two 6-volt storage batteries in parallel and a more sensitive control rheostat to heat the filament, instead of the 110-volt D.C. line, one terminal of which was grounded at the power house. The entire system was insulated from the earth except at one point to keep

the potential of the system as a whole constant. The heater coil around the plate was heated from the 220-volt D.C. line, which was earthed in the middle at the power house. When observations were taken with the current in the heater coil, all other points of the system were insulated from the ground, thereby getting rid of the electrical leak through the soap-stone insulation. This made it possible to study the effect of the temperature of the plate over any range desired above room temperature.

The purpose of these experiments was:

1. To determine the number of secondary electrons emitted from the plate per primary electron bombarding it as a function of the energy of impact, *i.e.*, the coefficient of secondary emission.

2. To determine the effect of the nature of the surface on the coefficient of secondary emission.

3. To measure the ionization potential of the surface and its variation with the nature of the surface.

4. To determine the effect of the temperature of the plate alone on the amount of secondary emission.

5. To test for high speed secondary or reflected electrons.

PART I.

The Coefficient of Secondary Emission as a Function of the Energy of Impact.

A curve showing this relation is given in Fig. 2, in which the abscissæ

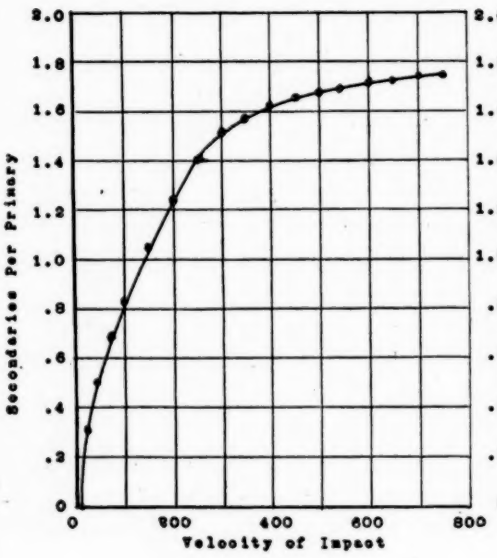

Fig. 2.

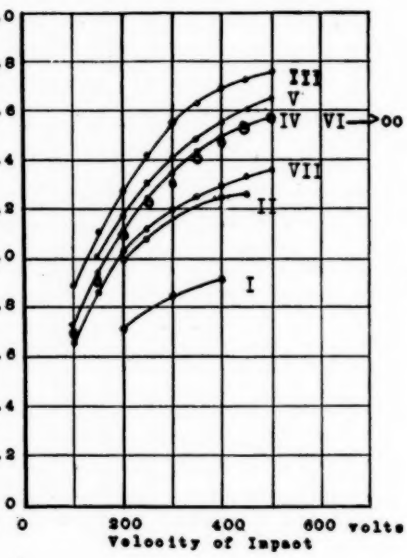

Fig. 3.

are the velocities of impact expressed in volts and the ordinates are the

numbers of secondaries per primary. In order to determine a point on this curve, *i.e.*, the number of secondaries per primary at any particular velocity of impact, a curve such as that shown in Fig. 4 may be used.

In Fig. 4, the shield s and plate p were kept at the same potential,

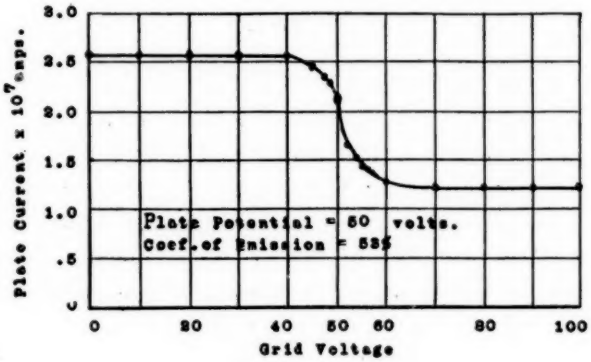

Fig. 4.

viz., 50 volts, and the grid g was varied from 0 to 100 volts (all voltages being taken with respect to the filament as zero). The current was measured by the galvanometer G_2 in the plate circuit. As the grid potential was varied from 0 to 40 volts, the plate current remained practically constant. This is because the slow electrons that were re-emitted from the plate could not traverse the retarding field between the plate and grid until that field became less than 10 volts. At that point the plate current starts to drop and continues to drop until the grid potential reaches about 70 volts or 20 volts higher than the plate. The coefficient of secondary emission is given by the ratio of the drop in plate current (a measure of the secondary current) to the value of the current at the upper level (a measure of the primary current). In this case it is 53 per cent.

It is not necessary to obtain a complete curve like Fig. 4 in order to get the points of the curve in Fig. 2. It can be done by giving the plate and shield a voltage corresponding to the velocity of impact desired and the grid a voltage sufficiently low to drive all the re-emitted electrons back to the plate. Then the plate current will give the upper level of Fig. 4, *i.e.*, the primary current. Next make the grid voltage sufficiently high to draw to it all secondary electrons that are emitted and take the plate current reading again. The first reading minus the second divided by the first will give the number of secondaries per primary. If these two readings are taken close together so that the filament temperature does not have a chance to change, this ratio

remains practically constant during a large number of observations at the same plate potential even though the filament temperature were allowed to change between sets of readings. The average of a large number of points obtained in this way gave the points of the curve in Fig. 2.

PART II.

The Effect of the Nature of the Surface.

The apparatus used in this experiment was employed to obtain various data over a period of about two years. During this time the plate was heated frequently by means of the heating coil in a vacuum in which the residual gas was air. At frequent intervals a curve such as in Fig. 2 was obtained. It was noticed that this curve was higher each successive time, indicating a larger secondary emission. This phenomenon is shown in Fig. 3. Curve I. represents some observations by Dr. Barber shortly after the apparatus was constructed. Curve II. was taken about three months later and curve III. after a period of about one and one half years. When the surface was such as indicated by curve III., it was noticed that the plate was covered with black spots directly in front of the holes in the grid. Assuming that these black spots were of copper oxide, the apparatus was filled with hydrogen, pumped down, and the furnace coil heated to a dull red heat for several hours, thereby changing the curve from III. to IV. The apparatus was heated repeatedly in air at a very low pressure for about a month. After this treatment the curve was raised to the position indicated by curve V. Another hydrogen treatment similar to the first one dropped the curve to VI., indicated by the circles. Curve VI. is almost in coincidence with curve IV., both being the result of the same treatment. This hydrogen treatment did not remove the spots completely.

A more severe treatment was given by heating in a rarified atmosphere of hydrogen for 30 hours with the heating coil white hot. This brought the curve down to VII. and the spots appeared to be entirely removed. On disassembling the apparatus, a slight trace of the spots could be seen, indicating that the reduction was not complete. The lack of complete reduction is also shown by the fact that curve VII. did not drop to the position near curve I., which was taken when the surface was clean copper.

These results indicate:

1. That the curves in this paper and also in Dr. Barber's are not for pure copper but rather for copper with a copper oxide coating.

2. The curves in Fig. 3 indicate that the coefficient of secondary emission is greater for copper oxide than for pure copper.

Plate Current = 10^{-7} amps.

3. If it is desired to obtain a larger number of secondaries per primary, copper oxide should be used instead of pure copper.

PART III.

The Ionization Potential and its Variation with the Nature of the Surface.

Figure 5 shows the type of curves used to determine approximately the ionization potential of the surface, *i.e.*, that potential of the plate with respect to the filament at which the low velocity secondary electrons begin to be emitted from the plate. If there be any high velocity reflected electrons present, these curves would not be affected by them. The ionization potential would be given by the point in Fig. 2 where the curve cuts the axis of abscissæ. Unfortunately this point is very difficult to determine accurately with this apparatus, because of the effect of the holes in the grid when the potential is low and because the number of secondaries per primary at that point is very small. Hence these results are not quantitative but qualitative and are probably not more accurate than within one volt of the correct value. Nevertheless they are accurate enough to show the variation caused by the oxide on the surface.

The curves in Fig. 5 are taken in the same manner as in Fig. 4 except

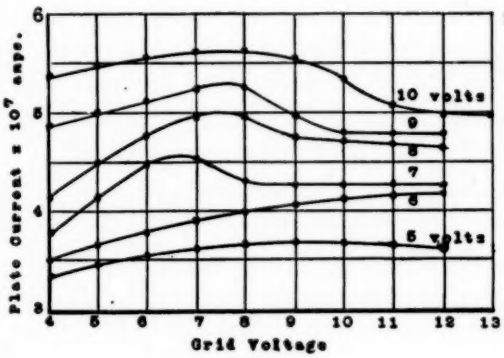

Fig. 5.

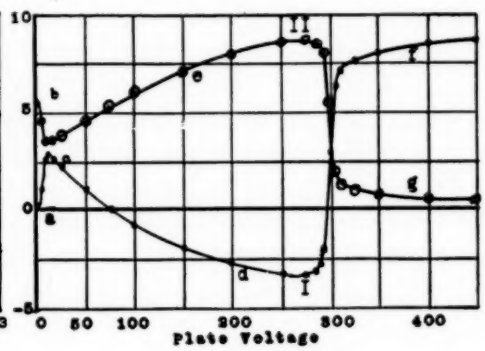

Fig. 6.

that the plate voltage is between 5 and 10 volts instead of 50. Observe that in Fig. 4 the curve starts to drop when the grid voltage is about 10 volts less than the plate voltage. That means that the fastest secondary electrons have sufficient speed to travel against a retarding field of 10 volts. In Fig. 5 one would expect that if there are any secondaries emitted from the plate at all, the curves should start to drop slightly before the grid voltage reaches that of the plate. The 5-volt curve (plate potential = 5 volts) and the 6-volt curve show no effect of

this kind, but the 7-volt and all the higher voltage curves do show this drop at the proper place. This indicates that the ionization potential is between 6 and 7 volts. These curves were taken for a surface condition represented by curve VII. of Fig. 3.

Table I. gives the ionization potential corresponding to different curves in Fig. 3 while the oxide was being formed and not after the hydrogen treatment.

TABLE I.

Ionization Potential.	Corresponding Curve in Fig. 3.
Between 6 and 7 volts.....	Curve VII.
" 8 " 9 "	" IV.
" 10 " 11 "	" III.

The following conclusions may be drawn:

1. As more oxide is produced on the surface the ionization potential increases and the number of secondaries per primary for higher velocities is also increased, as shown in Part II.

2. If the curves of Fig. 3 were to be produced to cut the axis of abscissæ, they would cross one another.

3. Copper oxide has a higher ionization potential and a correspondingly higher percentage of emission than pure copper.

PART IV.

The Effect of the Plate Temperature on the Amount of Secondary Emission.

In Dr. Barber's paper the coefficient of secondary emission was determined for different plate temperatures and it was found to decrease as the temperature increased up to about 100° C. At that time the electrical leak through the soap-stone insulation between the plate and heating coil increased very rapidly with the temperature and it was very difficult to make complete correction for this leak. The present experimental results were obtained with the entire system insulated from the earth, thus practically eliminating this leak. Table II. gives the results thus obtained with a plate voltage of 300 volts.

TABLE II.

Furnace Current (Amperes).	Estimated Temperature of Plate.	Coefficient of Secondary Emission.
0	25° C.	1.57
.4	100° C.	1.64
.7	300° C.	1.64
.9	450° C.	1.61

The results in Table II. indicate that there is no temperature effect.

PART V.

A Test for High Speed Electrons.

The curves of the type shown in Fig. 4 do not indicate definitely whether there exist high speed reflected electrons or not. They merely indicate, as stated by Millikan and Barber, that if such reflected electrons exist their number is not large. All of the curves of this type that have been taken have a practically level portion for grid voltages less than 10 volts below the plate voltage. When it is not level it always rises to the right. If there were a large number of electrons varying in speed from that of the primary electrons to that of the secondaries, the curve would fall to the right, exactly the opposite behavior to that observed. This is because as the retarding field between the plate and grid decreases, more of these high speed electrons would get over to the grid and thus decrease the plate current.

If the current through the grid circuit were observed, it ought to indicate those that strike the grid at all potentials. In this apparatus the shield and grid were separated by two porcelain rings, which were not good enough insulators. When the shield and grid were at different potentials the leak completely masked the effects to be observed.

Figure 6 shows an attempt to offset that difficulty. The grid and shield were kept at the same potential, viz., 300 volts, and the plate potential was varied from 0 to 450 volts with respect to the filament. The current that flowed through the plate circuit is given by curve I. The current through the grid circuit is given by curve II. A study of these curves gives the following conclusions:

1. At *a* on the curve, the electrons are accelerated by the field of 300 volts and retarded by the same field. They are therefore almost completely stopped, hence the plate current is zero.

2. At *b*, the electrons are stopped before they reach the plate and are drawn back to the grid, hence the high grid current.

3. The maximum point at *c* means that the reverse secondary current is increasing faster than the direct primary current.

4. At *d*, the secondary current is larger than the primary, hence the negative plate current. More electrons leave the plate than hit it.

5. This grid current indicates the secondary current. It increases when the plate current decreases. At *e*, the secondary current is large.

6. The plate current rises very high at *f*, because the field between the plate and grid is such as to stop all the secondaries and turn them back to the plate.

7. Since the grid current at *g* does not drop to zero, it indicates either

(1) that there is a leak through the insulation or (2) that there are high speed reflected electrons present which are not stopped by the retarding field. Since the grid and shield are at the same potential the first conclusion is quite improbable. Hence we may conclude that contrary to the preliminary indications obtained by Millikan and Barber[1] a few of the electrons are reflected with speeds comparable with those of the electrons impinging on the plate.

Conclusions.

The principal conclusions which may be drawn from this investigation are:

1. The number of secondaries per primary increases very rapidly with the velocity of impact for plate voltages between the ionization potential of the surface and 300 volts. For higher voltages the number increases more slowly but still continues to increase at 750 volts.

2. The parts of the plate directly in front of the holes in the grid gradually become coated with a thin layer of copper oxide. This oxide layer has a large effect on the amount of secondary emission; the thicker the layer the greater the emission. This may be because the copper oxide molecule contains more electrons than copper and hence an impinging electron has a better chance to knock out others from the surface.

3. The ionization potential is determined qualitatively and found to increase as the oxide layer becomes thicker.

4. The amount of secondary emission is not affected by the temperature of the plate up to 450° C.

5. There appear to be a few electrons that are reflected or re-emitted with velocities comparable with those of the primary electron stream.

In conclusion the author wishes to express his indebtedness to Professor R. A. Millikan for the problem and help in interpreting the data. Dr. I. G. Barber gave valuable instruction on the preliminary details of the experiment. Dr. H. G. Gale and Dr. A. J. Dempster have also given valuable suggestions and criticisms.

Ryerson Physical Laboratory,
University of Chicago,
August 31, 1922.

[1] At the time of the first preliminary report by Millikan and Barber upon experiments of this kind it was stated that the form of the plate curves obtained "seemed to show" the absence of reflected electrons, or that "if the phenomenon exist at all the number so reflected is negligible." The present experiments indicate that the phenomenon does exist, though the precise amount and the distribution with voltage of these reflected electrons are not yet known.

AN APPLICATION OF THE ELECTRON THEORY TO THE HALL EFFECT.

By John A. Eldridge.

Abstract.

Modified electron theory of the hall effect.—It is generally supposed that the simple electron theory of conduction leads to a negative coefficient for this effect and that the positive coefficients found for many metals are anomalous. But if we suppose the free path instead of the free time of motion of the electrons to be independent of the velocity, then in the *case of isotropic conductors*, the effect comes out zero. Considering the group of electrons having a given speed immediately after collision with molecules, those moving with the electric field E will be retarded and will be more deflected by a magnetic field H than those moving against E, giving a positive coefficient, but electrons moving at right angles to both E and H will give a negative coefficient, and assuming all directions equally probable, the resultant effect for each group and therefore for all is found to be zero. By slight modification of the assumptions of the simple theory, either positive or negative coefficients may be obtained. *In the case of a crystal*, on account of the asymmetry of free paths, a positive effect might be expected for one orientation and a negative for one at right angles. Though the experimental results are not as simple as this, the fact that the Hall effect has never been detected for mercury and that nearly all metals with negative coefficients have face-centered crystal lattices, while those with positive coefficients have body-centered or hexagonal lattices, indicates that the distribution of free paths with reference to E and H is of importance.

Modified electron theory of conductivity.—The same assumptions as to free path lead to the expression for specific conductivity which has been obtained by Lorentz and others. According to this theory, the electrons with velocities parallel to the field take no part in conduction, since the retarding effect on half of them balances the accelerating effect on the other half. In the case of a crystal, the conductivity should depend on the direction of the field with respect to the crystal axis, as in fact it does.

IN 1879 Hall discovered that when an electric current flows in a conductor in a transverse magnetic field, an electromotive force is produced which is at right angles both to the primary current and to the magnetic field. This is as we should expect, but the variation in sign which occurs in different metals has never been satisfactorily explained. Supposing the current to be due to the transportation of negative charge, we anticipate a negative value for the "Hall coefficient" and no excuse is apparent for the positive values which are found in many cases; it has been one of the outstanding failures of the electron theory that it has in no way cleared up the matter but has only made the earlier view more precise.

In the figure the electric field is supposed acting in the direction of

the x axis (*i.e.*, the force on the electron is in the negative x direction); the electronic current is flowing from right to left and the magnetic field is supposed directed outward from the paper. A fundamental law of electromagnetism tells us that upon a negative charge so moving in such a field a force is exerted tending to deflect the charge downward. This is all so simple that we are indeed shocked when we find experiment showing in many cases a deflection in the opposite direction. In the cases of bismuth, nickel, silver and other substances the electronic current is found deflected as it should be by the simple theory (in these cases the Hall coefficient is given a negative sign); but in an equally large number of cases (tellurium, antimony, iron, etc.) the deflection is found to be in the opposite direction. The enormous range which has been found in the absolute values of the coefficients also seems quite out of keeping with the theory. Tellurium and bismuth have by all odds the largest values for their Hall coefficients and in one case the value is positive and in the other it is negative. In most cases the effect is extremely small and there is no indication whatever of a preponderance of negative values among the elements.

The discord between the theory and the observed phenomena is made more striking when we remember how satisfactory the electromagnetic theory is when applied to other similar phenomena. In the case of conduction through gases which has furnished us with the model for our theory of metallic conduction, the deflection of the electron moving through a magnetic field is found to be quite in accord with the theory. And again in the cases of metallic conductors, it is of course true that whatever the effect on the electrons, the conductor as a whole when carrying a current in a magnetic field always is subject to a force which in direction and magnitude is quite in accord with the theory and depends not at all upon the material of the conductor. If this force is to be considered as the aggregate of the forces impressed upon the individual electrons, how is this to be brought into consistency with the Hall phenomenon?

With the aid of hypotheses introduced *ad hoc* the contradictions which the Hall effect seems to present may be explained away. Thomson has accounted for the effect by assuming the agency of intra-atomic magnetic fields; Riecke, Drude and others have hypothecated positive as well as negative carriers of electricity in metals;[1] but these hypotheses cannot be said to have met with general acceptance and have certainly been unfruitful in their effects upon the theory of metals. Collateral

[1] Thomson, Corpuscular Theory of Matter, Chap. V., and Drude, Ann. der Phys., 3, p. 369 (1900).

evidence seems significantly lacking for either hypothesis. Lorentz has raised serious objections to the theory of Drude. And yet the positive carrier theory does still exist as a competitor of the simple electron theory and bears evidence of the important place which the Hall effect has had in shaping the theory of conduction.

It is the purpose of this paper to show that the electron theory does not lead inevitably to a negative Hall coefficient as has been generally supposed but in its simplest form leads (to the same degree of approximation as that hitherto employed) to a zero coefficient. This still leaves the observed effect unexplained. It does however, and without introducing assumptions expressly for that purpose, show that our intuitive anticipation of a negative coefficient is not justified by the electron theory and so removes the phenomenon from the rather paradoxical position which it has hitherto occupied. It is not to be expected that this simple view of conduction can lead to a complete explanation of the phenomenon; but by slight modifications of the assumptions made in this paper, either positive or negative coefficients may be obtained and it seems reasonable to hope that with our increasing knowledge of metallic structure we may develop a less artificial theory of conduction which will account for many of the galvanomagnetic and thermomagnetic effects.

In the electron theory as usually developed it has been assumed that the *time* of free flight was not affected by the presence of the electric and magnetic fields. The electric field modifies the velocity of the electron and the assumption that the time of flight is unchanged tacitly involves the assumption that the free path of the electron is proportional to the velocity. No attempt seems to have been made to justify this assumption and indeed it appears to have been made unconsciously. It is surely more reasonable to assume that the free *path* rather than the free time is independent of the velocity. This is the assumption of this paper.

With this exception the assumptions made are quite conventional. Electrons are supposed moving with thermal velocities among fixed atomic centers and all directions are equally probable after reflection from an atomic center. The ratio of the electrical drift velocity to the thermal velocity is considered small.

During any interval of time there will occur in the conductor a large number of electronic reflections, in all directions and with thermal velocities ranging about a mean thermal velocity $\bar{v}_0$ and free paths ranging about a mean free path $\bar{\lambda}$. In most cases the conductor may be considered isotropic. Even though the metal consists of crystals, these crystals are arranged in random fashion among themselves so that in any reasonably large volume of the metal the mean free path (as well as the thermal velocity) will be the same in one direction as in another.

Of all the electrons in the conductor under consideration which have been reflected during an element of time, we first consider the contribution to the Hall effect only of those with some definite thermal velocity v_0 and free path λ. Representatives of this group are found in all parts of the conductor, going in all possible directions but all with the same thermal velocity and free path.

The free path here considered is the one which actually exists in the presence of the electric and magnetic fields and it is supposed that for an isotropic substance, even under these conditions, the number of electrons with free path λ and thermal velocity[1] v_0 is the same in all directions.

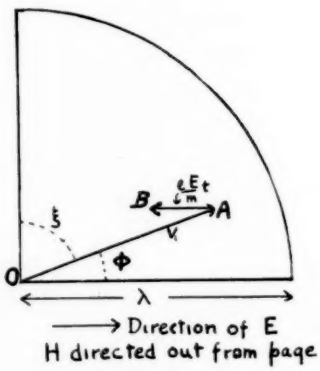

Fig. 1.

We first consider the deflection produced by a magnetic field upon a single representative of this group. The following notation applies:

n = number of electrons of this group reflected per cubic centimeter per unit solid angle per second.
T = time of free flight.
T_0 = time of free flight without the electric field.
v_0 = thermal velocity.
v_{0y} = y component of thermal velocity.
λ = free path of electron.
Y = total displacement in y direction during a free path.
e, m = the absolute value of the charge and mass of the electron.
E = electric field (directed to the right along the x axis of the figure).
H = magnetic field (directed out from the page in the figure).
ϕ = the angle between the path of the electron and x axis.
ξ = the angle between the path of the electron and y axis.
ψ = the angle between the path of the electron and the principal axis of the crystal.

Taking one electron of the v_0 group and referring to the figure, the

[1] That is, the velocity at the instant of reflection.

radius represents the free path λ, the constant vector OA and the variable vector AB represent, respectively, the thermal velocity v_0 and the velocity due to the electric field, that is $(eE/m)t$ in the negative x direction. The resultant velocity of the electron is the vector sum of v_0 and $(eE/m)t$.

The magnetic force on electrons in the y direction is

$$\frac{He}{c}\left(v_0 \cos\phi - \frac{eE}{m}t\right).$$

Hence

$$\frac{d^2y}{dt^2} = \frac{He}{cm}\left(v_0 \cos\phi - \frac{eE}{m}t\right)$$

and therefore the displacement of the electron in the y direction is

$$y = v_{0y}t + \frac{He}{2cm}\left(v_0 \cos\phi \cdot t^2 - \frac{1}{3}\frac{eE}{m}t^3\right). \tag{1}$$

The average velocity during the free path is

$$v_0 - \frac{eE}{2m}T_0 \cos\phi$$

and the free time therefore equals

$$T = \frac{\lambda}{v_0 - \frac{eE}{2m}T_0 \cos\phi} = T_0\left(1 + \frac{eE}{2mv_0}T_0 \cos\phi\right). \tag{2}$$

Substituting in (1)

$$Y = v_{0y}T_0\left(1 + \frac{eE}{2mv_0}T_0 \cos\phi\right) + \frac{HeT_0^2}{2cm}\left\{v_0 \cos\phi + \frac{eE}{m}T_0(\cos^2\phi - \tfrac{1}{3})\right\}$$

since we may neglect terms of the order of eE/mv_0 in the parenthesis multiplying $HeT_0^2/2cm$.

Considering now all electrons which belong to our group, which are of course travelling in all directions, we find that their contribution to the Hall current is

$$I_y = 2\pi \int_0^\pi neY \sin\phi \, d\phi.$$

Terms in v_{0y} drop out by symmetry with respect to the xz plane and so

$$I_y = \frac{\pi ne^2HT_0^2}{cm}\int_0^\pi \left\{v_0 \cos\phi + \frac{eE}{m}T_0(\cos^2\phi - \tfrac{1}{3})\right\} \sin\phi \, d\phi \tag{3}$$
$$= 0.$$

As this particular group gives a Hall current of zero, so will any other

group with velocity v_0' and free path λ' and the total Hall current from the theory is zero.

It will be instructive to point out qualitatively how the substitution of the constant path for the constant time hypothesis has led to this result. If we fix the attention on two electrons, moving respectively to the right and left along the x axis in the figure, the former (going against the current) will on the average be going slower than the one which is moving with the current, due to the retardation of the field during the time of free flight. The magnetic force is of course greater upon the more rapidly moving electron and in equal times this one would be deflected the more but *in the same path* the slower of two electrons is deflected the more by a magnetic field. Therefore if all electrons in the conductor were like these two, it would be those going *against* the field which would have the larger deflection and the substance would have a *positive* Hall coefficient. However when electrons with thermal velocities nearly normal to the direction of the applied electric field are considered the reverse is the case and these alone lead to a negative coefficient. In the case of isotropic substances where equal numbers travel in each direction and with similar distributions of free paths in each direction, the total effect has been shown above to be zero. If however in any particular case the free paths in the direction of the primary current were on the average longer than those at right angles thereto, the electrons going in this direction would be most deflected and such a conductor would under these circumstances have a positive coefficient. While it is difficult to see how this assymmetry of path can exist in the case of most conductors, it should be a factor in the case of a crystal and this case is examined more fully in the last part of this paper.

II.

The expression for the electrical conductivity of a metal as given by Drude is

$$\sigma = \frac{Ne^2\bar{\lambda}\bar{v}_0}{4\alpha\Theta}.$$

More recently errors in his derivation have been pointed out and the expression

$$\sigma = \frac{Ne^2\bar{\lambda}\bar{v}_0}{3\alpha\Theta}$$

is obtained [1] which goes over into the expression obtained by Lorentz

[1] Bohr "Dissertation," page 54; Swann, Phil. Mag., 27, p. 441 (1914); Livens, Phil. Mag., 29, p. 173 (1915). Mayer has recently summarized the literature on this subject [Jahab. Rad. und Elec. 18, p. 201 (1922)] but makes no reference to these papers.

if account is taken of the Maxwellian distribution of velocity among the electrons. This expression does not seem as yet to have displaced in the literature the one obtained by Drude. By a method quite similar to that used in the first part of this paper the expression for conductivity can be obtained. The method used seems to the writer somewhat simpler than those hitherto used for the derivation, and is interesting as showing that the correction which has been introduced above in the classical treatment of the Hall effect is essentially the same one as that which has already been applied to the treatment of conduction.

At first it will be convenient to neglect the distribution in the thermal velocities of the electrons and it will be supposed that they all have the mean velocity $\bar{v}_0$. As before all the electrons will be divided into groups having free paths λ_1, λ_2, λ_3, etc., and corresponding free times $T_{0,1}$, $T_{0,2}$, $T_{0,3}$, etc., in the absence of the field, which become altered to T_1, T_2, T_3, etc., by the influence of the field. The electric field is supposed directed along the x axis as before and X_1 represents the displacement in this direction of some electron of the first group during its free flight.

$$X_1 = -v_0 T \cos\phi + \frac{eET^2}{2m},$$

$$= -v_0 T_0 \cos\phi + \frac{T_0^2 eE}{2m}\sin^2\phi,$$

substituting in the value of T from (2) and dropping higher order terms as before. To get the contribution to the current from all electrons of the first group we must integrate for all directions

$$I_1 = 2\pi e \int_0^\pi X_1 n_1 \sin\phi \, d\phi, \qquad (4)$$

$$= \frac{4\pi n_1 e^2 T_{0,1}^2 E}{3m},$$

where I_1 is the current contribution of all electrons in the first group and n_1 is the number of electronic collisions per second, per cubic centimeter, per unit solid angle producing electrons which belong to this group.

The total current then is equal to

$$\frac{4\pi e^2 E}{3m}\sum_1^\infty n_1 T_1^2 = \frac{4\pi e^2 E \nu \overline{T_0^2}}{3m} = \frac{8\pi e^2 E \nu \overline{T_0}^2}{3m},$$

where $\overline{T_0^2}$ and $\overline{T_0}^2$ represent the mean value of the square and the square of the mean, respectively, and ν is the total number of collisions per second per cubic centimeter per unit solid angle, which occur. It has been assumed here that the probability of a free path of any particular

length is an exponential function of the free path (or free time); *i.e.*, $dn = \nu e^{-T} dT$. It is well known that in such a case the mean value of T^2 is twice the square of the mean value T, which accounts for the factor 2 which has been introduced in the last member of the above equality.

Let N represent the number of free electrons per c.c. of the conductor, and $\alpha\Theta$ the energy of thermal agitation per molecule at the temperature Θ

$$4\pi\nu = \frac{N\bar{v}_0}{\lambda} = \frac{N}{T_0}$$

$$I = \frac{2}{3}\frac{Ne^2\bar{T}_0 E}{m} = \frac{Ne^2\bar{\lambda}\bar{v}_0 E}{3\alpha\Theta},$$

and the expression for the specific conductivity is

$$\sigma = \frac{Ne^2\bar{\lambda}\bar{v}_0}{3\alpha\Theta}, \tag{5}$$

which is identical with the expression obtained by Swann.[1]

Swann has shown that if account be taken of the variation in the thermal velocities among the electrons the above expression reduces to the expression which has been obtained by Lorentz.

The expression (5) differs from that of Drude with which it is comparable by a factor of 4/3. A factor 2 has been introduced by taking account of the difference between the mean of the free path squared and the square of the mean free path, and a factor 2/3 introduced by taking the free path rather than the free time as unchanged by the field. In Drude's theory all electrons contributed equally to the current regardless of the direction in which they were moving; in the present treatment it is seen that those electrons which move in a direction parallel to the field take no part in the conduction. Electrons moving forward are accelerated, it is true, and those moving backward are retarded but as each has the same free path this can produce no displacement of electricity.

The significance of the different numerical factor which is introduced into the classical expression for conduction is probably not great. More significant is the dependence of the conductivity upon the direction of the impressed field in the case of an anisotropic substance (such as a crystal) which the present theory leads us to expect. As has been pointed out, those electrons which move in directions parallel to the impressed field play no part in the conduction. In a crystal the distances between atoms are different in different directions. The deflections which the

[1] Phil. Mag., S. 6, Vol. 27, pp. 441–455, 1914.

electrons suffer in the field are proportional to the squares of the free paths, and so the crystal should show greater conductivity when it is so oriented that the longer free paths lie in directions normal to the field and so become the paths of those electrons which play a part in conduction, than when these longer paths lie parallel to the field. It is well known that in crystals the conductivity is indeed a function of the direction of the impressed field.

III.

In the consideration of the Hall effect it has been assumed that the substance was isotropic. In many cases, however, the mean value of λ (or T_0) must be different in different directions. It may be supposed that although the theory given offers no explanation for the observed effect in isotropic substances, it may throw some light on the phenomena which have been observed in the case of a crystal. The theory is far from agreeing with the experimental results, but because of the prominent position which this model of the conductor has occupied and because the emphasis which the theory places upon distribution of free paths may indeed suggest a more satisfactory explanation, the theory will be extended to cases where λ is not considered an isotropic function.

In the case of a crystal with symmetrically placed atoms, the free path must be fairly constant for a given direction but changing very suddenly with slight changes in direction. A smoothed-over value of λ will here be considered which is thought of as a function of ψ, the angle between the principal crystal axis and the direction vector. n may also be thought to depend upon the relative position of the atoms and so also to be a function of ψ.

Under these conditions T_0 and n must remain under the integration sign and expression (3) is so modified as no longer to equal zero. The expression for the Hall coefficient, R, may be obtained. By definition

$$R = \frac{E_y}{Hi_x}, \tag{6}$$

where E_y is the electrical field intensity in the y direction applied in experiment to neutralize the Hall current, and i_x the primary current density.

Upon equation (3) one integration has already been performed which was possible because of the symmetry of n and T about the x axis. Now that this symmetry no longer exists, since n and T_0 are functions of ψ as well as of ϕ, equation (3) must be changed to the form

$$I_y = \frac{e^2H}{2cm}\int \left\{ nT_0^2v_0 \cos\phi + nT_0^3\frac{eE}{m}(\cos^2\phi - \tfrac{1}{3}) \right\} d\omega,$$

where the integration is to be carried throughout the total solid angle of which $d\omega$ is an element. The first term in the integrand drops out as before. A similar change is made in equation (4) and the expression for the current due to E_y is then equated to the Hall current.

$$-\frac{e^2E_y}{2m}\int nT_0^2 \sin^2\xi\, d\omega = \frac{e^3HE_x}{2cm^2}\int nT_0^3(\cos^2\phi - \tfrac{1}{3})d\omega.$$

Equation (6) then becomes when we substitute the value of i_x

$$R = \frac{E_y}{Hi_x} = \frac{2\int nT_0^3(\cos^2\phi - \tfrac{1}{3})d\omega}{ce\int nT_0^2 \sin^2\phi\, d\omega \cdot \int nT_0^2 \sin^2\xi\, d\omega}$$

or in terms of the observed conductivities σ_y and σ_x

$$R = \frac{e^3}{2\sigma_y\sigma_x cm^2}\int nT_0^3(\cos^2\phi - \tfrac{1}{3})d\omega. \qquad (7)$$

If the principal axis of the crystal is parallel to the primary electric field

$$R = \frac{\pi e^3}{\sigma_y\sigma_x cm^2}\int_0^\pi nT_0^3(\cos^2\phi - \tfrac{1}{3})\sin\phi\, d\phi.$$

Under these conditions the integration will give R a positive value if nT_0^3 has a larger value in directions near the principal axis than in directions perpendicular thereto, and a negative value if the opposite be the case.

If, on the other hand, the current be flowing in a plane normal to the principal axis, the Hall coefficient should from the nature of equation (7) have an opposite sign to that in the preceding case.[1] The value in this case may vary somewhat, depending on the direction of the magnetic field relative to the principal axis. Considering only the case in which the magnetic field is perpendicular to the crystal axis, it is seen that the value of the product $\sigma_y\sigma_x$ is the same as in the case just discussed (where the electric field was parallel to the crystal axis). If nT_0^3 be supposed to have its largest value along the crystal axis, the integrated quantity in (7) will have a smaller value in the present case, making the Hall coefficient different in absolute value as well as in sign from the case first discussed.

Comparing these results with the observations of Everdingen[2] for

[1] Supposing nT_0^3 to have its larger value in the direction of the principal axis, if this axis is in the plane perpendicular to the x axis in the figure, nT_0^3 will on the average have larger values when $\phi = \pi/2$ than when $\phi = 0$ or π. Since $\cos^2\phi - 1/3$ is negative for these values (and its unweighted mean value is 0) the average value of $nT_0^3(\cos^2\phi - 1/3)$ must be negative.

[2] Comm. Leiden No. 61. See also Lownds, Ann. d. Phys., 9, p. 677 (1902).

bismuth it will be seen that the theory as developed is not competent to account for the observed phenomena. The table gives the values of the coefficients found for electric and magnetic fields parallel to and perpendicular to the crystal axis.

Hall Coefficient for Bismuth with Magnetic Field of 4,600 Gauss.

Electric Field.	Magnetic Field.	
	⊥	||
||	− 8.0	
⊥	−10.6	−0.2
⊥	− 8.8	−0.0
⊥	− 8.2	+0.6

Values are given for the electric field in several directions perpendicular to the crystal axis. The resistance was found to be $\sqrt{5/3}$ greater along the principal axis than perpendicular thereto. It is seen that the direction of the magnetic field is very important; the important rôle assigned by the theory to the direction of the electric field is not in agreement with the experiment.

Many data have been obtained for the effect of temperature upon the Hall effect. In the case of bismuth in particular, this effect is very remarkable, but a comparison with the theory in this case will not be made. As is well known, the simple theory gives the wrong temperature coefficient for resistance and until this matter can be cleared up it is hardly profitable to apply it to the varied effects of temperature upon the Hall coefficient.

The increase of the coefficient observed in exceedingly thin plates is directly predicted by the theory. The asymmetry of the free paths on the surface should have an important effect and the relative importance of this surface phenomenon increases as the thickness decreases. The parallelism which is in general to be observed between resistance and the magnitude of the Hall effect is anticipated by the present theory as it was indeed by the older application of the electron theory.

Not only were the theories unable to account for the positive Hall coefficients but until recently it could be said that the variation in sign of these coefficients was paralleled by no other known property of the material. Today we find a very remarkable parallelism between this sign and the crystal structure. With but two or three doubtful exceptions, we find the positive coefficient in metals with body-centered cubic or hexagonal close packed lattices while those metals with face-centered cubic lattices have negative coefficients. A very obvious effect of the

crystal structure will be an alteration of the relative free path lengths in different directions, and it is the importance of this path distribution which the above theory tends to emphasize.

The Hall effect has never been detected in mercury. Experimental difficulties make this result of doubtful value, but if it be accepted, we find here in a liquid conductor where the isotropism is more truly realized than in a crystalline substance a check with the theory.

It has been the main purpose of this paper to show that by a reasonable application of the same electron theory which has been applied to explain conduction the paradox of the Hall effect disappears. Hitherto it has been felt, intuitively, that a current of negative electrons should lead to a negative Hall coefficient and the electron theory has done nothing to weaken this belief. The electron theory is now shown to contradict this belief. The unreality of the theory, with its substitution of conventionalized assumptions for an intimate knowledge of intra-atomic fields, does not at all vitiate its conclusion that any presumption which has been made as to sign of the effect has been unjustified. Since in the above case a null effect was derived, by slight modification of hypotheses either a positive or negative may be obtained.[1] A hitherto unknown emphasis is laid upon the importance of the distribution of paths of the electron in the conductor. The remarkable parallelism which exists between the crystal structure as determined by x-ray analysis and the sign of the Hall effect seems to the author to strengthen the probability that this path distribution holds the key to the effect. The theory given is obviously unsatisfactory, but it at least seems suggestive of a possible explanation of the phenomena when a more exact mechanism of conduction is formulated.

UNIVERSITY OF WISCONSIN,
August 25, 1922.

[1] If we assume, for instance, that the electron retained after collision some of its directed velocity acquired in the electric field, we should obtain a *positive* coefficient.

PRECISION MEASUREMENTS OF CRYSTALS OF THE ALKALI HALIDES.

By Wheeler P. Davey.

Synopsis.

Crystal structure and dimensions for all the alkali halides.—The Hull powder method of obtaining x-ray diffraction patterns was used. By comparing each diffraction pattern directly with the pattern of NaCl simultaneously recorded on the other half of the film, the grating space of each crystal powder was measured in terms of the side of the unit cube of NaCl, assumed to be 2.814 A, with a precision of about 0.1 per cent. The average results for the sides of the unit cubes are as follows:

	Li.	Na.	K.	Rb.	Cs.
Fluorides.....	2.007	2.310	2.664	3.663	3.004
Chlorides.....	2.566	Assumed	3.138	3.267	4.118
Bromides.....	2.745	2.968	3.285	3.418	4.287
Iodides.....	3.537	3.231	3.525	3.655	4.558

The arrangement of the ions is simple cubic except for RbF, CsCl, CsBr and CsI for which it is body-centered cubic. The relative intensities of the lines reflected from various planes and the corresponding computed interplanar distances are tabulated for each halide. It was observed that Cs and I ions are as equal in diffracting power as are the atoms of Mo, Ta and W, which crystallize with the same structure as CsI, and that K and Cl ions also have equal diffracting power.

Crystal densities of all the alkali halides, computed from x-ray data.—The results, accurate to within about 0.3 per cent, are as follows, assuming the density of NaCl to be 2.163:

	Li.	Na.	K.	Rb.	Cs.
Fluorides.....	2.646	2.809	2.534	3.504	4.617
Chlorides.....	2.069	Assumed	1.990	2.859	3.973
Bromides.....	3.463	3.246	2.768	3.415	4.453
Iodides.....	2.494	3.665	3.125	3.557	4.523

For the chlorides and iodides, except LiI, the values agree with those obtained by other methods within 0.2 per cent on the average, whereas for the others the values are higher by 0.5 to 1.5 per cent for the bromides and 1 to 9 per cent for the fluorides.

THE results of the measurements of crystals of the alkali halides have been presented from time to time at the meetings of the American Physical Society. It is the purpose of the present article to record these results in a form suitable for reference. The apparatus used has already been sufficiently described.[1] The method was the well-

[1] Davey, A New X-ray Diffraction Apparatus. Journ. Opt. Soc. Am., V., 479 (1921); General Electric Review **25**, 565, (1922)

known Hull powder method. The opacity of the crystals to x-rays was decreased by diluting the crystal powder with flour or cornstarch. By simultaneously recording the x-ray diffraction pattern of NaCl on one half of the film, and the pattern of the crystal under investigation on the other half of the same film, it is possible to determine the dimensions of the second crystal in terms of the dimensions assumed for NaCl. The side of the unit cube of NaCl was taken as 2.814 A, following Duane.[1]

TABLE I.

CsI.

Plane.	Intensity.	Interplanar Distance.			
		(1)	(2)	(3)	(4)
1 1 0	100	3.23	3.23	3.21	3.23
1 0 0	40	2.28	2.28	2.28	2.28
2 1 1	80	1.858	1.862	1.862	1.862
1 1 0 (2)	25	1.613	1.614	1.612	....
3 1 0	30	1.440	1.443	1.441	1.442
1 1 1	6	1.317	1.318	1.316	1.318
3 2 1	25	1.217	1.220	1.219	1.218
1 0 0 (2)	3	1.139	1.140	....	....
4 1 1 1 1 0 (3)	6	1.074	1.076	1.074	1.076
2 1 0	4	1.016	1.018	1.019	1.019
3 3 2	4	.970	.971	.970	.972
2 1 1 (2)	3	.929	.930	.930	....
4 3 1 5 1 0	6	.894	.894	.893	....
5 2 1	3	.830	.831	....	....
1 1 0 (4)	1	....	....	....	....
5 3 0 4 3 3	3	.780	.781	....	....
1 0 0 (3) 2 2 1	1	....	....	....	....
6 1 1 5 3 2	2	.738	.740	....	....
Side of unit cube		4.553	4.560	4.559	4.561

CsI.—Diffraction pattern, body-centered cubic.

Crystal structure, body-centered cube of ions. $d = 4.558 \pm .005$ A.

Distance of closest approach of $\overset{+}{Cs}$ and $\overset{-}{I}$, $- 3.947$ A.

Density { from x-ray data, $- 4.523 \pm .014$. / from literature, $- 4.509$.

The lines in the diffraction pattern, especially those which are nearest the zero-line, have a shape roughly like that of the cross section of some part of a plano-concave or convex-concave lens, since the source of the pattern is a line instead of a point. The reading of each line was taken at a point corresponding to the center of the "lens." No accuracy is

[1] Duane, Bulletin of the National Research Council, Vol. 1, part 6, No. 6 (1920).

claimed for lines caused by planes having a spacing of more than 2.00 A. Every line which corresponded to an inter-planar distance of 2.00 A or less was made to give a value for the side of the unit cube by multiplying the interplanar distance by the appropriate theoretical ratio. The values

TABLE II.

CsBr.

Plane.	Intensity.	Interplanar Distance. (1)	Interplanar Distance. (2)
1 0 0	1	4.33	....
1 1 0	100	3.03	3.03
1 1 1	¾	2.42	....
1 0 0 (2)	10	2.15	2.14
2 1 0	¾	1.925	....
2 1 1	35	1.750	1.750
1 1 0	7	1.520	1.516
2 2 1 1 0 0 (3)	½	1.431	....
3 1 0	5	1.356	1.355
3 1 1	¼	....	....
1 1 1 (2)	1½	1.240	1.239
3 2 0	¼	....	....
3 2 1	3½	1.148	1.147
1 0 0 (4)	¾	1.073	....
4 1 0 3 2 2	¼	....	....
4 1 1 1 1 0	1½	1.011	1.010
3 3 1	....	....	....
2 1 0 (2)	¾	.957	....
4 2 1	....	....	....
3 3 2	¾	.914	....
2 1 1 (2)	¾	.875	....
4 3 0 1 1 1 (5)	....	....	....
4 3 1 5 1 0	1½	.841	.840
Side of unit cube		4.288	4.287

CsBr.—Diffraction pattern, simple cubic. The strong lines form a body-centered cubic pattern.

Crystal structure, body-centered cube of ions, $d = 4.287 \pm .004$ A.

Distance of closest approach of $\overset{+}{Cs}$ and $\overset{-}{Br}$, 3.713 A.

Density { from x-ray data, 4.453 ± .013. / from literature, 4.433.

so obtained from any one film were clustered about some one value according to the probability law. For a given kind of crystal the most probable value of the side of the unit cube (measured graphically)[1] differed from film to film by not more than 0.1 per cent from the mean

[1] Whipple, Journ. Franklin Inst., 182, 37–205 (1916).

except in the case of LiF, where the variation was less than 0.2 per cent from the mean.

As a check on the results, the densities of the crystals were calculated from the x-ray data and compared with the densities ordinarily found in the literature. Wherever possible the values are those given by Baxter

TABLE III.

CsCl.

Plane.	Intensity.	Interplanar Distance. (1)	Interplanar Distance. (2)
1 0 0	1½	4.2	4.2
1 1 0	10	2.90	2.92
1 1 1	1	2.38	2.38
1 0 0 (2)	1½	2.05	2.06
2 1 0	1½	1.840	1.848
2 1 1	3	1.681	1.681
1 1 0 (2)	1½	1.454	1.458
2 2 1 / 1 0 0 (3)	1	1.372	1.373
3 1 0	1½	1.303	1.303
3 1 1	½	1.238	1.241
1 1 1 (2)	¾	....	....
3 2 0	½	....	....
3 2 1	2	1.102	1.102
1 0 0 (4)	½	....	....
4 1 0 / 3 2 2	½	.999	.997
4 1 1 / 1 1 0 (3)	¾	.972	.971
3 3 1	....	....	....
2 1 0 (2)	½	.921	.919
4 2 1	½	.897	....
3 3 2	½	.877	....
2 1 1 (2)	¼	....	....
4 3 0 / 1 0 0 (5)	½	....	....
4 3 1 / 5 1 0	½	.806	.806
Side of unit cube		4.116	4.120

CsCl.—Diffraction pattern, simple cubic.

Crystal structure, body-centered cube of ions. $d = 4.118 \pm .004$ A.

Distance of closest approach of $\overset{+}{Cs}$ and $\overset{-}{Cl}$, 3.566 A.

Density { from x-ray data, 3.973 ± .012. / from literature, 3.974

and Wallace at 25° C.[1] Other sources are specifically mentioned when used. Since the calculated densities are free from errors in weighing due to voids and to the presence of moisture, they may be expected to

[1] Baxter and Wallace, Journ. Am. Chem. Soc., 38, 260 (1916). These authors give references to the earlier determinations. Further references may be found in Groth's Chemische Krystallographie, Vol. 1 (1906).

be more accurate than most of the currently accepted densities. If the crystal data are accurate to 0.1 per cent, the calculated densities should be correct to 0.3 per cent. In the calculation of the densities, the mass associated with each unit of atomic weight was taken to be 1.649×10^{-24} grams.[1]

TABLE IV.

CsF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	10	3.47	3.48
1 0 0	15	2.99	3.01
1 1 0	15	2.12	2.13
3 1 1	8	1.812	1.815
1 1 1 (2)	4	1.735	1.736
1 0 0 (2)	2	1.502	1.501
3 3 1	3	1.379	1.381
2 1 0	5	1.342	1.341
2 1 1	2½	1.227	1.225
5 1 1 / 1 1 1 (3)	3	1.157	1.158
1 1 0 (2)	½	....	1.062
5 3 1	1½	1.016	1.017
1 0 0 (3) / 2 2 1	1	1.001	1.001
3 1 0	½	.950	.948
5 3 3	1	....	.917
3 1 1 (2)	1	....	.905
1 1 1 (4)	½	....	.868
7 1 1 / 5 5 1	¾	....	.839
3 2 0	....	....	....
3 2 1	¾	....	.803
5 5 3 / 7 3 1	¾	....	.782
1 0 0 (4)	½	....	.751
7 3 3	....	....	....
4 1 0 / 3 2 2	½	....	.728
Side of unit cube		6.006	6.008

CsF.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.004 \pm .003$ A.

Distance of closest approach of $\overset{+}{Cs}$ and $\overset{-}{F}$, 3.004 A.

Density { from x-ray data, $4.617 \pm .014$. / from literature, 4.38 (H. E. Merwin, quoted by Wyckoff and Posenjak, Jl. of Wash. Acad. Sci., **12**, 248, 1922).

In the case of the elements, the intensities of the lines in the diffraction patterns depend upon the effects of temperature, absorption, size of crystals, distribution of electrons, variation of reflecting power with

[1] Davey, Science, Nov. 18, 1921.

TABLE V.

RbI.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	1	4.24	4.25
1 0 0	7	3.69	3.69
1 1 0	2	2.59	2.55
3 1 1	½	2.21	2.20
1 1 1 (2)	1	2.12	2.11
1 0 0 (2)	½	1.828	1.830
3 3 1	½	....	....
2 1 0	1	1.636	1.635
2 1 1	1	1.493	1.491
5 1 1 and 1 1 1 (3)	½	....	....
1 1 0 (2)	½	1.292	....
5 3 1	½	....	....
1 0 0 (3) and 2 2 1	½	1.218	1.217
3 1 0	½	1.156	....
5 3 3	½	1.101	....
3 1 1 (2)	½	....	....
1 1 1 (4)	½	....	....
7 1 1 and 5 5 1	½	1.014	....
3 2 0	½	.976	....
Side of unit cube		7.310	7.309

RbI.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 3.655 \pm .004$ A.
Distance of closest approach of Rb^+ and I^-, $-$ 3.655 A.
Density: from x-ray data, $3.557 \pm .011$; from literature, 3.550.

TABLE VI.

RbBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 0 0	15	3.41	3.45
1 1 0	10	2.41	2.42
1 1 1	3	1.970	1.975
1 0 0 (2)	1	1.703	1.706
2 1 0	3	1.527	1.530
2 1 1	2	1.396	1.393
1 1 0 (2)	½	1.211	....
2 2 1 and 1 0 0 (3)	1	1.140	....
3 1 0	½	1.083	....
3 1 1	½	1.030	....
Side of unit cube		3.418	3.417

RbBr.—Diffraction pattern, simple cubic.
Crystal structure, simple cube of ions. $d = 3.418 \pm .003$ A.
Distance of closest approach of Rb^+ and Br^-, 3.418 A.
Density: from x-ray data, $3.415 \pm .010$; from literature, 3.349.

TABLE VII.

RbCl.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	2	3.77	3.77
1 0 0	3	3.25	3.25
1 1 0	2	2.29	2.30
3 1 1	½	1.971	1.970
1 1 1 (2)	1	1.890	1.884
1 0 0 (2)	¾	1.633	1.635
3 3 1	½	1.497	....
2 1 0	1	1.463	1.462
2 1 1	¾	1.333	1.333
Side of unit cube		6.536	6.534

RbCl.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.267 \pm .003$ A.

Distance of closest approach of $\overset{+}{Rb}$ and $\overset{-}{Cl}$, 3.267 A.

Density { from x-ray data, 2.859 ± .009.
from literature, 2.798 (Baxter and Wallace).
2.806 – 2.827 (Groth, Chemische Krystallographie).

TABLE VIII.

RbF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 0 0	10	3.69	3.66
1 1 0	8	2.61	2.59
1 1 1	2	2.12	2.11
1 0 0 (2)	1	1.840	1.835
2 1 0	3	1.639	1.638
2 1 1	1½	1.496	1.492
1 1 0 (2)	¾	1.292	1.290
{ 2 2 1 / 1 0 0 (3)	1	1.219	1.220
3 1 0	¾	1.159	1.157
3 1 1	½	....	1.105
1 1 1 (2)	½	....	....
3 2 0	½	....	....
3 2 1	¾	.979	.979
Side of unit cube		3.665	3.661

RbF.—Diffraction pattern, simple cubic.

Crystal structure, body-centered cube of ions. $d = 3.663 \pm .004$ A.

Distance of closest approach of $\overset{+}{Rb}$ and $\overset{-}{F}$, – 3.172 A.

Density { from x-ray data, 3.504 ± .010.
from literature, 3.202 (Van Nostrand's Chem. Annual).

angle, and the number and grouping of the coöperating planes. In the case of compounds, the intensities depend also upon the relative number of electrons in the atoms or ions. For instance, Cs^+ and I^- have the same number of electrons, and act identically, within experimental error. The pattern is that of a body-centered cube. In CsBr, the Br^- has fewer electrons than the Cs^+. The reflection from Br^- is weaker than that from Cs^+, so that the diffraction pattern of CsBr is that of a body-centered cube of strong lines, with weaker lines added which change the

TABLE IX.

KI.

Plane.	Intensity.	Interplanar Distance.		
		(1)	(2)	(3)
1 1 1	2	4.07	4.07	4.07
1 0 0	8	3.53	3.53	3.53
1 1 0	6	2.49	2.49	2.49
3 1 1	2	2.13	2.13	2.13
1 1 1 (2)	3	2.04	2.04	2.04
1 0 0 (2)	1½	1.763	1.764	....
3 3 1	1	1.620	....	1.620
2 1 0	4	1.578	1.576	1.577
2 1 1	3	1.442	1.439	1.440
5 1 1 / 1 1 1 (3)	¾	1.356	1.355	1.358
1 1 0 (2)	1	1.247	....	....
5 3 1	½	1.194	....	....
1 0 0 (3) / 2 2 1	1	1.172	1.174	1.176
3 1 0	1	1.114	1.114	1.115
5 3 3	¼	....	....	....
3 1 1 (2)	¾	1.061	1.061	....
1 1 1 (4)	½	....	....	....
7 1 1 / 5 1 1	¾	....	....	....
3 2 0	½	....	....	....
3 2 1	1	.940	.941	.941
Side of unit cube		7.050	7.045	7.054

KI.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 3.525 \pm .004$ A.
Distance of closest approach of $\overset{+}{K}$ and $\bar{I}$, 3.525 A.
Density { from x-ray data, 3.125 ± .009. / from literature, 3.123.

pattern into that of a simple cube. In CsCl, since the number of electrons in Cl^- is still less than in Br^-, the interference is still less complete, so that those lines which were faint in the case of CsBr are considerably stronger in the diffraction pattern of CsCl.

The accuracy with which the intensities of lines in a diffraction pattern

can be estimated from a photographic film is low. The rate at which energy is received by the film is so small that the ordinary exposure law no longer holds. Small changes in blackness often represent large changes in incident energy. For this reason no numerical estimate of x-ray intensities has been made, but the blackness of each line on the photographic film is expressed in terms of an arbitrary scale of 100. If a comparison is desired of the relative intensities of the lines in the patterns of two substances, both patterns should be taken on the same film and should have about the same range of exposure. Equality of exposure times for the same exposure-range may be obtained by diluting the more active specimen with flour or cornstarch.

TABLE X.

KBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	2	3.78	3.80
1 0 0	10	3.27	3.30
1 1 0	9	2.32	2.32
3 1 1	1½	1.975	1.982
1 1 1 (2)	5	1.895	1.901
1 0 0 (2)	1½	1.638	1.643
3 3 1	¾	1.510	....
2 1 0	6	1.465	1.470
2 1 1	3	1.343	1.343
5 1 1 / 1 1 1 (3)	1½	....	....
1 1 0 (2)	¾	1.162	....
1 0 0 (2) / 2 2 1	1	1.096	1.095
3 1 0	1	1.036	1.039
3 1 1 (2)	½	.989	.990
3 2 1	½	....	.879
Side of unit cube		6.564	6.576

KBr.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 3.285 \pm .003$ A.
Distance of closest approach of $\overset{+}{K}$ and $\overset{-}{Br}$, 3.285 A.
Density { from x-ray data, $= 2.768 \pm .008$. / from literature, $= 2.749$.

Certain lines were so faint on some of the films that no accurate reading of the inter-planar distance could be made. In such cases an estimate was made of the blackness of the line in terms of the arbitrary scale, as an indication that the line was actually present in the diffraction pattern.

CsI.—This was a sample obtained from the Chemical Laboratory of the University of Illinois. The pattern is of the body-centered cubic

type. The density shows that the arrangement of ions is also body-centered cubic. This is the arrangement to be expected for close-packing of equal numbers of oppositely charged spheres. Table I. shows the data taken from three films. One of these was read twice with a time interval of about three months between readings. Both readings (1 and 2 in the table) are given to show how nearly the readings may be duplicated. Two other films, not shown in the table, were taken in which the NaCl calibration was replaced by the diffraction patterns of Mo and Ta

TABLE XI.

KCl.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 0 0	15	3.12	3.13
1 1 0	10	2.21	2.21
1 1 1	3	1.812	1.814
1 0 0 (2)	1	1.567	1.575
2 1 0	2½	1.403	1.404
2 1 1	1½	1.281	1.281
1 1 0 (2)	½	1.110	....
2 2 1			
1 0 0 (3)	1	1.045	1.046
3 1 0	½	.991	.992
3 1 1	½	.944	.946
1 1 1 (2)	½	.905	....
3 2 0	½	.869	....
3 2 1	½	.838	.839
Side of unit cube		3.136	3.140

KCl.—Diffraction pattern, simple cubic.
Crystal structure, simple cube of ions. $d = 3.138 \pm .003$ A.
Distance of closest approach of $\overset{+}{K}$ and $\overset{-}{Cl}$, 3.138 A.
Density { from x-ray data, 1.990 ± .006.
from literature, 1.987.

respectively for the purpose of comparing the intensities of the various lines. These films show that the relative intensities of the lines of CsI, Mo and Ta are identical within experimental error. Since the marshalling of ions in CsI is identical with the marshalling of atoms in Mo and Ta, the equality of intensities shows that, within experimental error, Cs^+ and I^- are as equal in diffracting power as the atoms of Mo or of Ta. The value 4.558 ± .005 A assigned to the side of the unit cube of CsI

agrees well with the value 4.562 A reported by Clark and Duane.[1] As far as is known to the writer these values represent the only attempts to date to obtain a precision measurement of the cube of CsI.

TABLE XII.

KF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	1½	3.11	3.09
1 0 0	10	2.69	2.67
1 1 0	8	1.887	1.882
3 1 1	1	1.609	....
1 1 1 (2)	2	1.539	1.538
1 0 0 (2)	1	1.333	1.334
3 3 1	¾	1.222	....
2 1 0	2½	1.192	1.193
2 1 1	1½	1.087	1.088
5 1 1			
1 1 1 (3)	½	1.024	....
1 1 0 (2)	½	.939	....
5 3 1	½	.900	....
1 0 0 (3)	¾	.887	....
2 1 1			
3 1 0	¾	.842	....
5 3 3	½	....	....
3 1 1 (2)	¾	.803	....
1 1 1 (4)	½	....	....
7 1 1			
5 5 1	½	....	....
3 2 0	½	....	....
3 2 1	¾	.711	....
Side of unit cube		5.327	5.330

KF.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 2.664 \pm .003$ A.
Distance of closest approach of $\overset{+}{K}$ and $\overset{-}{F}$, 2.664 A.
Density { from x-ray data, 2.534 ± .008.
from literature, 2.35 – 2.48 (Groth, Chemische Krystallographie).
2.454 (Van Nostrand's Chem. Annual).

CsBr.—This was made by treating the iodide with HBr in the presence of H_2O_2. The CsBr was crystallized out from aqueous solution. Readings are tabulated from two films.

[1] Clark and Duane, Phys. Rev. **20**, 85, (1922).

CsCl.—This was made by treating the iodide with HCl in the presence of H_2O_2. The CsCl was crystallized out from aqueous solution. Readings are tabulated from two films, one of which had more exposure than the other. All the lines of the fainter film match the theoretical simple cubic pattern. The more strongly exposed film shows four additional

TABLE XIII.

NaI.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	4	3.74	3.75
1 0 0	6	3.24	3.24
1 1 0	5	2.29	2.29
3 1 1	4	1.953	1.954
1 1 1 (2)	2	1.864	1.870
1 0 0 (2)	1½	1.615	1.619
3 3 1	2	1.486	1.485
2 1 0	3	1.448	1.445
2 1 1	2½	1.319	1.319
5 1 1 / 1 1 1 (3)	1½	1.245	1.244
1 1 0 (2)	1	1.145	1.142
5 3 1	1	1.096	1.093
1 0 0 (3) / 2 2 1	1	1.077	1.077
3 1 0	1	1.022	1.020
5 3 3	½	.987	.986
3 1 1 (2)	¾	.973	.972
1 1 1 (4)	½	....	....
7 1 1 / 5 5 1	½	.905	.904
3 2 0	½	.897	.895
3 2 1	½	.864	.862
7 3 1 / 5 5 3	½	.841	.840
1 0 0 (4)	....	....	....
7 3 3	....	....	....
4 1 0 / 3 2 2	½	.782	....
1 1 0 (3) / 4 1 1	½	.761	....
Side of unit cube		6.466	6.460

NaI.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 3.231 \pm .003$ A.
Distance of closest approach of $\overset{+}{Na}$ and $\overset{-}{I}$, 3.231 A.
Density { from x-ray data, 3.665 ± .011. / from literature, 3.665.

faint lines. As nearly as could be measured, these corresponded to interplanar distances of 2.26, 2.15, 1.94 and 1.89 A. They are probably due to a trace of impurity, as they are also present as faint lines on a badly overexposed film mentioned below under CsF.

CsF.—Attempts to make CsF from Cs_2CO_3 according to the directions given in Gmelin-Kraut gave an almost amorphous mass. Prolonged exposure gave only a general fog on the film with a few faint lines, some of which were mentioned above under CsCl. The lines showed interplanar spacings of 3.18, 2.60, 2.26, 2.15, 1.94, 1.89, 1.83 and 1.42 A as nearly as could be determined. The general fog was so great and the lines were so faint that no accuracy can be claimed for the readings. The CsF was so hydroscopic that it was difficult to keep it water-free.

TABLE XIV.

NaBr.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	2½	3.45	3.45
1 0 0	8	2.98	2.98
1 1 0	10	2.10	2.10
3 1 1	3	1.791	1.788
1 1 1 (2)	3	1.714	1.711
1 0 0 (2)	1	1.483	1.485
3 1 1	1	1.363	1.359
2 1 0	3	1.329	1.325
2 1 1	2	1.213	1.213
5 1 1			
1 1 1 (3)	2	....	1.144
1 1 0 (2)	½	1.049	1.049
5 3 1	½	1.005	....
1 0 0 (3)			
2 2 1	1	.989	.988
3 1 0	1	.938	.938
5 3 3	½	....	....
3 1 1 (2)	½	....	....
1 1 1 (4)	½	....	....
7 1 1	½	....	....
5 5 1			
3 2 0	½	....	....
3 2 1	½	.794	....
Side of unit cube		5.939	5.932

NaBr.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 2.968 \pm .003$ A.
Distance of closest approach of $\overset{+}{Na}$ and $\overset{-}{Br}$, 2.968 A.
Density { from x-ray data, 3.246 ± .010.
from literature, 3.203.

An effort was made to suck up molten CsF into a glass specimen tube. The melting point of the CsF was above the softening point of the glass, so that it was not possible to fill the tube. A sample of CsF obtained from the Geophysical Laboratory through the kindness of Dr. Sosman and Mr. Posenjak gave results tabulated in Table IV. This sample is from the same lot of salt as that used by Posenjak and Wyckoff.[1]

[1] Posenjak and Wyckoff, Jour. Wash. Acad. Sci., **12**, 248, (1922).

RbI.—This was a sample bought from Merck. The data from two films are tabulated in Table V.

RbBr.—This was made from the iodide in the same manner as CsBr. All the Rb salts and all bromides give considerable fog on the films due

TABLE XV.

NaCl.

Plane.	Intensity.	Theoretical Interplanar Distance (d_{NaCl}, = 5.628).
1 1 1	3	3.249
1 0 0	100	2.814
1 1 0	90	1.990
3 1 1	¾	1.697
1 1 1 (2)	15	1.625
1 0 0 (2)	4	1.407
3 3 1	¾	1.291
2 1 0	20	1.259
2 1 1	10	1.149
5 1 1		
1 1 1 (3)	½	1.083
1 1 0 (2)	2	.995
5 3 1	½	.951
1 0 0 (3)		
2 2 1	2½	.938
3 1 0	2	.890
5 3 3	1	.858
3 1 1 (2)	¾	.848
1 1 1 (4)	¼	.812
7 1 1		
5 5 1	....	.788
3 2 0	½	.780
3 2 1	1	.752
5 5 1		
7 3 1	....	.733
1 0 0 (4)	....	.703
7 3 3	....	.688
4 1 0		
3 2 2	1	.602
Side of unit cube		5.628

NaCl.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. "*d*" is assumed to be 2.814 A.
Density { on the basis of d = 2.814 A, 2.163.
from literature 2.161 (Baxter and Wallace).
2.167 – 2.188 (Groth, Chemische Krystallographie).

to fluorescent characteristic rays of Rb or Br which are strongly excited by the α lines from Mo. In the case of RbBr this fog is especially bad. The fog limits the number of lines which can be accurately measured on the diffraction pattern.

RbCl.—This was made from rubidium alum in the ordinary way by treating the alum with HCl and $BaCl_2$, and then removing Ba and Al by means of NH_4OH and $(NH_4)_2CO_3$. The RbCl was crystallized out from aqueous solution.

TABLE XVI.

NaF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	½	....	....
1 0 0	15	2.33	2.32
1 1 0	10	1.636	1.632
3 1 1	½	....	....
1 1 1 (2)	2	1.335	1.337
1 0 0 (2)	1	1.158	1.155
3 3 1	½	....	....
2 1 0	2	1.033	1.034
2 1 1	1	.943	.944
5 1 1 / 1 1 1 (3)	....	....	....
1 1 0 (2)	½	.815	.816
5 3 1	....	....	....
1 0 0 (3) / 2 2 1	¾	.769	.768
3 1 0	¾	.730	....
5 3 3	....	....	....
3 1 1 (2)	½	.696	....
Side of unit cube		4.620	4.622

NaF.—Diffraction pattern, ordinarily appears to be simple cubic. Prolonged exposure gives additional lines which complete the pattern of a face-centered cube of double the cube size.

Crystal structure, simple cube of ions. $d = 2.310 \pm .002$ A.

Distance of closest approach of $\overset{+}{Na}$ and $\overset{-}{F}$, $-$ 2.310 A.

Density { from x-ray data, 2.809 ± .008. / from literature, 2.558 (Groth), 2.766 (Van Nostrand's Chem. Annual).

RbF.—This was made from the chloride in the same manner as CsF. It was, however, nicely crystalline. Results are given in Table VIII. It should be noted that the arrangement of the ions in the crystal differs from that of the other Rb halides. The evidence of the diffraction pattern is, however, so definite that there is no chance of error in the interpretation. It would be interesting to see if RbF would show a simple-cubic structure at higher temperatures.

KI, KBr, KCl, KF.—These were obtained from stock. The original sources are unknown. All four salts crystallize as simple cubes of ions. The value 3.525 ± .004 A assigned to the side of the unit cube of KI agrees well with the value 3.532 A reported by Duane and Clark.[1] KI,

TABLE XVII.

LiI.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	3	4.10	4.13
1 0 0	15	3.58	3.58
1 1 0	10	2.51	2.51
3 1 1	2	2.13	2.14
1 1 1 (2)	3	2.05	2.04
1 0 0 (2)	1½	1.771	1.775
3 3 1	1	1.621	1.625
2 1 0	2	1.582	1.584
2 1 1	2	1.442	1.446
5 1 1	¾	1.362	1.365
1 1 1 (3)			
1 1 0	¾	1.249	1.252
5 3 1	¾	1.195	1.196
1 0 0 (3)			
2 2 1	1	1.178	1.181
3 1 0	½	1.117	1.120
5 3 3	½	....	1.080
3 1 1 (2)	½	1.064	1.068
1 1 1 (4)	½	1.020	1.025
7 1 1	½	....	.987
5 5 1			
3 2 0	....	....	....
3 2 1	¾	.944	.945
5 5 3	½	....	....
7 3 1			
1 0 0 (4)	½	....	....
7 3 3	½	....	....
4 1 0	½	.856	....
3 2 2			
Side of unit cube		7.066	7.083

LiI.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 3.537 \pm .005$ A.

Distance of closest approach of $\overset{+}{Li}$ and $\overset{-}{I}$, − 3.537 A.

Density { from x-ray data, 2.494 ± .015. from literature, 3.485 − 4.061 (Groth, Chemische Krystallographie).

KBr and KF give face-centered cubic patterns because the positive and negative ions do not act as equal diffracting centers. KCl gives a simple cubic pattern—*i.e.*, K^+ and Cl^- act as practically equivalent diffracting

[1] Duane and Clark, Phys. Rev. **20**, 84, (1922).

centers.[1] KCl is comparatively transparent to the rays employed and gives little fluorescent radiation to fog the film. It gives beautifully clear films with strong lines. One film was therefore given double the normal exposure so as to see whether any faint lines could be detected which would show a slight difference in the diffracting power of K^+ and Cl^-. No such lines could be found. It therefore seems safe to assume that the diffracting powers of K^+ and Cl^- are actually equal. Data for the potassium halides are given in Tables IX., X., XI. and XII.

TABLE XVIII.

LiBr.

Plane.	Intensity.	Interplanar Distance.		
		(1)	(2)	(3)
1 1 1	5	3.19	3.18	3.16
1 0 0	5	2.75	2.74	2.75
1 1 0	2	1.939	1.940	1.939
3 1 1	5	1.654	1.656	1.657
1 1 1 (2)	1	1.584	....	1.586
1 0 0 (2)	¾	1.373	....	....
3 3 1	2	1.260	1.261	1.258
2 1 0	1	1.228	1.228	1.227
2 1 1	1	1.124	1.120	1.119
5 1 1				
1 1 1 (3)	1	1.057	....	1.057
1 1 0 (2)	....	....	....	....
5 3 1	¾	.928	....	....
1 0 0 (2)	¾	.914	....	....
2 2 1				
3 1 0	½	.868	....	....
Side of unit cube		5.490	5.491	5.488

LiBr.—Diffraction pattern, face-centered cubic.

Crystal structure, simple cube of ions. $d = 2.745 \pm .003$ A.

Distance of closest approach of $\overset{+}{Li}$ and $\overset{-}{Br}$, 2.745 A.

Density { from x-ray data, 3.463 ± .010.
from literature, 3.464 (Baxter, J. Am. Ch. Soc., 1904).

NaI, NaBr, NaCl, NaF.—These salts were from stock. The original source is unknown. The NaCl used for calibrating was free from K and Mg. NaF ordinarily gives a simple cubic pattern, since the Na^+ and F^- are nearly equal in diffracting power. Prolonged exposure, however, shows that the complete pattern is face-centered-cubic, and the numerical results are tabulated on that basis. Data for the sodium halides are given in Tables XIII., XIV., XV. and XVI.

[1] See also W. H. and W. L. Bragg, "X-rays and Crystal Structure."

LiI.—This was made by treating Li_2CO_3 with HI. The resulting product was then evaporated to dryness in vacuo over H_2SO_4. Remaining traces of water and some of the free iodine were removed by washing in absolute alcohol. The rest of the free iodine was removed by grinding the crystals of LiI under amyl acetate. The salt was so hydroscopic that it had to be handled entirely under amyl acetate, even when filling the glass specimen tube. The specimen tube therefore contained LiI, flour and amyl acetate. Results are given in Table XVII.

TABLE XIX.

LiCl.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	40	2.96	2.98
1 0 0	40	2.55	2.58
1 1 0	20	1.814	1.821
3 1 1	15	1.549	1.551
1 1 1 (2)	3	1.482	1.484
1 0 0 (2)	1½	1.281	1.283
3 3 1	2	1.178	1.179
2 1 0	3	1.147	1.149
2 1 1	2	1.044	1.048
5 1 1 1 1 1 (3)	2	.985	.988
1 1 0 (2)	½	....	....
5 3 1	1	.866	.869
1 0 0 (3) 2 2 1	1½	.854	.855
3 1 0	1	.810	.812
5 3 3	½	....	....
3 1 1 (2)	½	....	....
1 1 1 (4)	½	....	....
7 1 1 5 5 1	½	.718	....
Side of unit cube		5.127	5.137

LiCl.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 2.566 \pm .003$ A.]
Distance of closest approach of $\overset{+}{Li}$ and $\overset{-}{Cl}$, 2.566 A.
Density {from x-ray data, 2.069 ± .006.
from literature, 2.068 – 2.074 (Groth, Chemische Krystallographie).

LiBr.—A sample of salt labeled LiBr gave a simple cubic pattern of side 4.008 A. Since this does not check even approximately the published density of LiBr, it was assumed that either the salt was not LiBr or that it was not anhydrous. The salt was therefore fused and then ground with flour under amyl acetate. It was soluble in the amyl acetate. The solution was then concentrated with heat and was sucked up into one end of a specimen tube. It solidified on cooling. The other end of

the tube was filled with NaCl as usual. No diffraction pattern of LiBr was obtained. Results from a second sample of salt are given in Table XVIII. This sample was sent me by Dr. Sosman of the Geophysical Laboratory. It is from the same lot of salt as that used by Posenjak and Wyckoff.[1]

LiCl.—This was obtained from Li_2CO_3 by the action of HCl. The salt was crystallized from aqueous solution. Results are given in Table XIX.

LiF.—This was obtained from stock. The origin is unknown. Results are tabulated in Table XX.

TABLE XX.

LiF.

Plane.	Intensity.	Interplanar Distance.	
		(1)	(2)
1 1 1	40	2.31	2.29
1 0 0	60	2.00	2.004
1 1 0	40	1.422	1.417
3 1 1	3	1.211	1.209
1 1 1 (2)	3	1.161	1.159
1 0 0 (2)	1½	1.006	1.000
3 3 1	1	.920	.919
2 1 0	2½	.899	.896
2 1 1	2	.821	.819
5 1 1 / 1 1 1 (3)	½	....	....
1 1 0 (2)	½	.710	....
5 3 1	½	.679	....
1 1 0 (3) / 2 2 1	1	.670	....
3 1 0	½	.636	....
Side of unit cube		4.020	4.008

LiF.—Diffraction pattern, face-centered cubic.
Crystal structure, simple cube of ions. $d = 2.007 \pm .004$ A.
Distance of closest approach of $\overset{+}{Li}$ and $\overset{-}{F}$, $-$ 2.007 A.
Density { from x-ray data, 2.646 ± .016.
from literature, $-$ 2.295 (Groth, Chemische Krystallographie).
2.601 (Van Nostrand's Chemical Annual).

It is a pleasure to acknowledge the assistance of Mr. C. G. Van Brunt and of Dr. D. Hall Brophy, of this laboratory, in the preparation of many of the salts, and of Miss M. K. Slattery and Mrs. J. L. Luedemann in the experimental work.

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September, 12, 1922.

[1] Posenjak and Wyckoff, Jour. Wash. Acad. Sci., **12**, 248, (1922).

OPTICAL PROPERTIES OF SOME METALLIC SULFIDES.

By E. P. T. Tyndall.

Abstract.

Optical constants of molybdenite (MoS_2) and stibnite (Sb_2S_3) in the visible region, 420 mμ to 740 mμ.—*The reflectivity* of a cleavage surface at 20° incidence was found to range from 0.35 to 0.60 (Figs. 2 and 3). At 45° incidence, the values are the same for MoS_2, but slightly less for Sb_2S_3. When cooled to about − 160° C., MoS_2 shows the selective bands enhanced and shifted toward the violet (Fig. 6), while Sb_2S_3 showed no change. *Transmission of two thin specimens of MoS_2*, 6.3 and 9.6 μ thick, increases rapidly as the infra-red is approached (Fig. 7). From these measurements the extinction modulus $n\kappa$ is computed. Cooling by liquid air was found to shift the transmission curve about 40 $m\mu$ toward the violet. *Indices of refraction and of extinction* were determined by allowing plane polarized light of azimuth 135° to fall on the crystal surface and analyzing the elliptically polarized light reflected. The method and apparatus are described in detail. For MoS_2, n and κ were obtained for light in the direction of the optic axis (Fig. 12). Anomalous dispersion is shown, n having a maximum value at 620 $m\mu$ (5.3) and minima at 595 and 655 $m\mu$. The extinction index lies between 0.2 and 0.4, with two maxima indicating selective absorption bands at 603 and 665 $m\mu$. For Sb_2S_3, two principal indices were obtained for light incident normal to the cleavage plane. Both refractive indices reach maximum values at 510 $m\mu$ (5.5 and 4.8), while both extinction indices increase steadily with decreasing wave-length. Reflectivities computed from these values of n and κ agree in general with those observed directly, but are somewhat higher throughout the middle of the spectrum. In the case of MoS_2 no variation of the optical properties with the age of the surface was observed, but with Sb_2S_3, fresh cleavage surfaces were used as the surface soon changed after exposure to the air. The metallic luster of these sulfides is due to the high refraction, the absorption being considerably lower than for metals.

Reflectivity of cleavage surfaces of pyrite (FeS_2) and of galena (PbS) in the visible region, 420 mμ to 740 mμ, was measured for an incidence of 20 °(Figs. 4 and 5). For 45° incidence, pyrite gives slightly lower values. Cooling with liquid air did not change the results for pyrite; galena was not tried.

CERTAIN of the metallic sulfides in the natural mineral state have very interesting optical properties. These have been studied by Koenigsberger and Reichenheim,[1] Coblentz,[2] Crandall,[3] and Coblentz and Kahler,[4] working in the infra-red region, and by Horn,[5] Drude,[6] and

[1] J. Koenigsberger, Phys. Zeits., 4, p. 495, 1902–03. J. Koenigsberger and O. Reichenheim, Centralblatt f. Min., p. 454, 1905.

[2] Coblentz, Pub. 65, Carn. Inst., p. 91. Pub. 97, Carn. Inst., pp. 13, 41.

[3] Crandall, Phys. Rev. (2), 2, p. 343.

[4] Coblentz and Kahler, B. S. Sci. Pap. No. 338.

[5] Horn, N. Jahrb. f. Min. Geol. u. Pal. Beil., Bd. 12, p. 269, 1898–99.

[6] D ude, Ann. d. Phys. u. Chem., 34, p. 489, 1888.

Müller[1] in the visible region of the spectrum. The work in the infra-red has consisted of determinations of spectral reflectivity, spectral transmission, and, in some cases, of the index of refraction from the spacing of the interference bands formed when light is transmitted or reflected by a thin film. In the visible region measurements have been made of the index of refraction and extinction index by studying the nature of the elliptically polarized light reflected from the surface of the crystal when the incident light is plane polarized. These will be referred to in detail later.

The work reported here consists mainly of determinations of the spectral reflectivities and of the indices of refraction and extinction indices of stibnite (Sb_2S_3) and molybdenite (MoS_2). Spectral reflectivities, however, were also obtained for galena (PbS) and pyrite (FeS_2). Previous work has shown that both stibnite and molybdenite have a high index of refraction, high reflectivity, great transparence in the infra-red, and an almost metallic absorption in the visible region of the spectrum. The regular spectral reflection was studied first.

1. Reflection at Room Temperature.

A Lummer-Brodhun spectrophotometer with contrast field was used. The wave-length calibration was made in the usual way with known spectral lines and, for the far red, Hartmann's[2] dispersion formula was used as a check. The arrangement of the apparatus is shown in Fig. 1(*a*).[3] A gas-filled tungsten lamp, *L*, served as a source for both collimators. By means of the lens, *ll'*, light was concentrated on the ground glass screen, *GG'*, in front of the variable slit, *S*. Lens *LL'* served to concentrate the light on the magnesium carbonate block, *BB'*. Either the standard mirror or the specimen being studied was placed at *MM'*. The standard was a small piece of silver-backed plate glass mirror. Its reflectivity was determined in absolute measure by comparison with a freshly prepared, chemically deposited silver surface. The values of the reflectivity of the latter as given in the Smithsonian Physical Tables[4] were assumed.

A determination of reflectivity was made by placing the standard mirror at *MM'*, Fig. 1(*a*), and observing the width of the variable slit, *S*, for a match at each wave-length setting. The standard was then replaced by the specimen and the observations repeated at the same

[1] Müller, N. Jahrb. f. Min. Geol. u. Pal. Beil., Bd. 17, p. 187, 1903.

[2] J. Hartmann, Astrophys. Jour., 8, p. 218, 1898.

[3] The photometric cube, dispersing prism, and observing telescope are not shown in the figure, but had the usual position relative to the collimators shown.

[4] Smith. Phys. Tab., p. 288 (1920).

wave-lengths, slit S' being kept at 0.2 mm. The ratio of the reflectivity of the specimen to that of the standard was then given by the ratio[1] of the slit-widths in the second case to those in the first. The absolute reflectivity of the specimen was then computed. The use of a variable slit has little to recommend it except convenience of operation and ease of making computations. Its reliability here was checked by transmission measurements made with another Lummer-Brodhun spectrophotometer, for which the variable slit method was known to hold, and with an infra-red spectrophotometer,[2] which used relative galvanometer deflections.

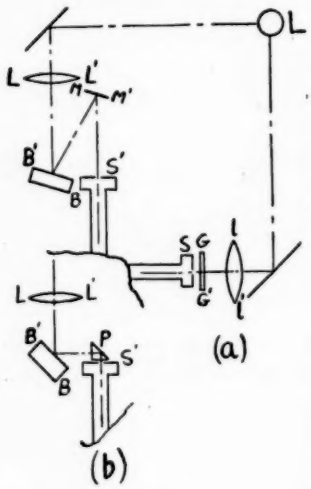


Fig. 1.

Arrangement of apparatus for measuring spectral reflectivity (*a*) at 20° incidence, (*b*) at 45° incidence.

An observer looking through the ocular slit and through the slit S' sees the surface of the carbonate block as imaged in the mirror MM'. In order to secure proper adjustment, that is, to see always the same part of the block in the field, a black, opaque diaphragm, pierced with a small hole, was placed in front of the carbonate. The mirror, MM', was then adjusted until the small spot of light was seen in the center of the field. This adjustment was made at the beginning of every determination, the diaphragm being removed while readings were being taken and then swung back into place at the end of the determination, to make sure that no shift had occurred. The diaphragm was left in place while changing from the standard to the specimen. For specimens which departed considerably from plane surfaces the spot of light, seen through the diaphragm, was irregularly shaped and somewhat spread over the field. It still seemed, however, to locate the best position of MM'. The field, when the diaphragm was removed, was always filled and was quite uniform for the better specimens. Check readings were taken at 550 and 600 mμ with LL' removed, in which case the illumination of BB' was uniform. The angle of incidence was about 20°, which was as

[1] Actually 0.02 mm. was subtracted from each slit-width before the ratio was computed. See Nichols and Merritt, PHYS. REV., 31, p. 502, 1910; and Karrer and Tyndall, B. S. Sci. Pap. No. 389, pp. 380–382.

[2] The transmission of an amber glass was measured by Dr. J. R. Collins on the infra-red set-up and by the writer on the Lummer-Brodhun instrument, covering the spectral region 720–530 mμ.

near to perpendicular incidence as the arrangement of apparatus would permit.

For measurement of reflection at 45° incidence a small right angle glass prism, *P*, Fig. 1(*b*), was used as a standard. The readings on the specimen were made with it in the position formerly occupied by the hypothenuse face of the prism. The pierced diaphragm was used as before for adjustment. The prism was assumed to have a reflectivity of 0.92 throughout the spectrum. This method was especially convenient for carrying the readings to the extreme red and blue since the light could then be very considerably concentrated on *BB'*.

Molybdenite.—Determinations were made on two specimens of molybdenite, both of which were obtained from Dr. Coblentz, of the Bureau of Standards. Specimen *A* was a thin, flat lamina stuck on plate glass. It had an excellent, plane, mirror-like surface, which must have been at least a year old at the time these measurements were taken. Specimen *B* had a freshly prepared surface, made by splitting some of the material with a razor. It was not so nearly plane as *A*, but the method of making the reflection measurements made this unessential. Each specimen had, of course, a natural cleavage surface, which in this mineral is probably perpendicular[1] to the optic axis. In Curve *A*, Fig. 2, is plotted the

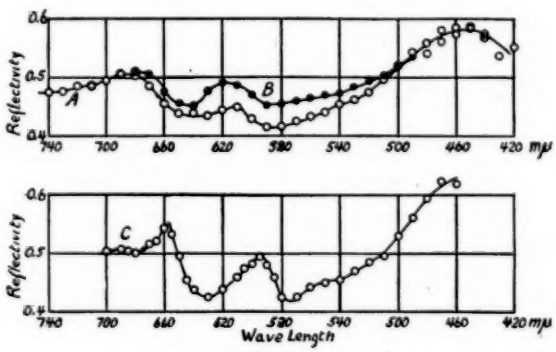


Fig. 2.

Molybdenite: Curve *A*, observed reflectivity room temperature, 20° and 45° incidence; Curve *B*, reflectivity computed from n and κ for perpendicular incidence; Curve *C*, observed reflectivity of specimen placed over liquid air, 20° incidence.

average of six determinations from 710–440 mμ, three of these being on specimen *A* at 20° incidence, two on specimen *B* at 20° incidence, and one on specimen *B* at 45° incidence, and the average of three determinations on specimen *A* at 45° incidence covering the spectral regions 690–740 mμ and 480–420 mμ. The agreement between all these different

[1] Crandall, loc. cit., pp. 355–6.

determinations was well within experimental errors. It must be noticed that the old surface had the same reflectivity as the new and that there was no appreciable change between reflectivity at 20° and 45° incidence.

Stibnite.—Several samples of Japanese stibnite were very kindly given the writer by Dr. Coblentz. This mineral may be split readily and the natural cleavage surface is almost plane and highly polished. Two specimens were used. Specimen *A* had been split some time before the readings were taken. Specimen *B* was prepared just before the first determination and showed no appreciable change in reflectivity during the period covered by the determinations. Two determinations were made on specimen *B* at 20° incidence. These are plotted in Fig. 3, Curve *A*. One determination of the reflectivity of specimen *B* at 45° incidence was made, covering the region 710–450 mμ, and one covering the regions 680–740 and 500–420 mμ. These are shown by Curve *B*, Fig. 3. The reflectivity at 45° incidence differs slightly from that at 20°

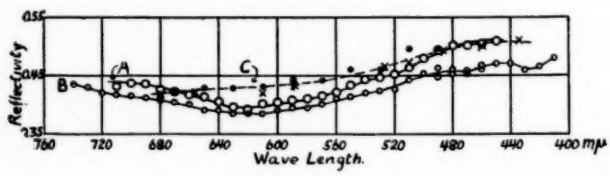


Fig. 3.

Stibnite: Curve *A*, observed reflectivity, 20° incidence; Curve *B*, observed reflectivity, 45° incidence; Curve *C*, reflectivity computed from n_1, κ_1 and n_2, κ_2, ● from writer's values, × from Müller's values.

incidence. The results for specimen *A* are not given as its reflectivity at 20° incidence was considerably below that for the fresh surface of specimen *B*. Previous work[1] has shown that a stibnite surface alters soon after cleavage. This will be referred to again later.

Galena.—Determinations were made on two specimens, *A* having an old surface, while *B* was split just before making the determination. The results of one determination on specimen *B* at 20° incidence are shown by Curve *A*, Fig. 4. The reflectivity computed from Horn's[2] and Drude's[3] values of the refractive index and extinction index are plotted as solid circles in Fig. 4. This material does not split with a very smooth surface so that the photometric field was rather poor. No determinations were made at 45° incidence. The determinations on specimen *A* are not plotted since the reflectivity was low, this mineral having also undergone a surface change of some kind.

[1] Drude, loc. cit.

[2] Horn, loc. cit.

[3] Drude, Ann. d. Phys., 36, p. 532, 1889.

Pyrite.—Determinations were made on the reflectivity of one sample of pyrite, which was loaned by Dr. Coblentz. It was in the shape of a parallelopiped with one plane face about 5 x 10 mm. which was used for the observations. No freshly split surface was available, but the surface

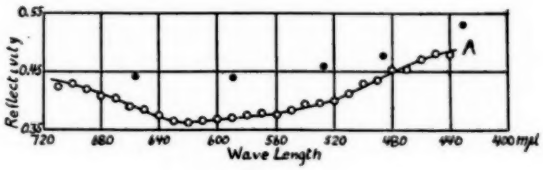


Fig. 4.

Galena: Curve *A*, observed reflectivity; ● reflectivity computed from n and κ of Horn and Drude.

used was lightly polished with a chamois before using. The results for 20° and 45° incidence are shown in Fig. 5. Curve *A* is the average of two determinations at 20° incidence and *B* of three determinations at 45° incidence.

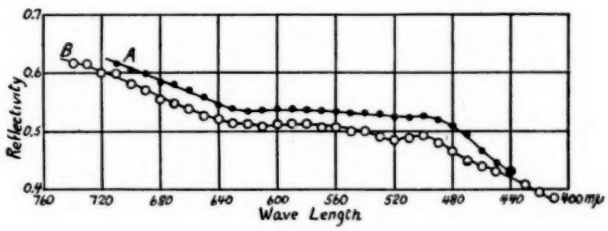


Fig. 5.

Observed reflectivity of pyrite: Curve *A*, 20° incidence, Curve *B*, 45° incidence.

2. Reflectivity of Molybdenite at Low Temperatures.

Previous observers[1] have found that the absorption coefficient, index of refraction, and photo-conductivity effect all change for molybdenite at low temperatures. It seemed likely, therefore, that there would be a change in the reflectivity also. To test this a specimen of molybdenite was placed in the position *MM'*, Fig. 1(*a*), in a clear glass Dewar flask. Readings were taken of the width of slit *S* throughout the spectrum; then these readings were repeated after liquid air had been poured into the flask, and again repeated after the air had evaporated and the specimen had returned to room temperature. In this manner the reflectivity at low temperatures was compared with that at room temperature, so that the absolute reflectivity for low temperatures could be determined. In Fig. 2, Curve *C*, is shown the result of one determination, the temperature having been measured, in this case, by means of a thermo-couple

[1] Crandall, loc. cit. Coblentz and Kahler, loc. cit.

placed adjacent to the specimen. Liquid air was introduced into the Dewar from time to time by means of a paper funnel. The temperature varied from − 155° C. to − 170° C. Several sets of readings were taken at each wave-length setting and at 550 mμ a number of sets were taken, as this served as a sort of a check point and readings were always taken at this point after every five or six sets of readings at other wave-lengths. Several other such determinations were made, all of which were in substantial agreement with this one. In Fig. 6 is plotted a

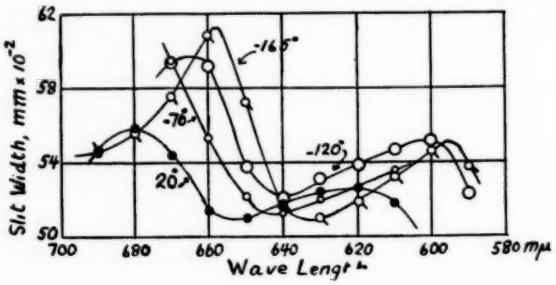


Fig. 6.
Molybdenite: Width of variable slit, *S*, at various temperatures.

curve of the observed widths of slit *S*, readings being taken at intervals as the specimen warmed up. The approximate temperature is shown on each curve. This shows the shifting of the bands with changing temperature.

Stibnite and pyrite showed no appreciable change in reflectivity at low temperatures. Galena was not tried.

3. Transmission of Molybdenite.

The spectral transmissions of two thin specimens (from Coblentz) were determined in the red end of the spectrum. To obtain readings to as long a wave-length as 780 mμ it was necessary to rearrange the apparatus somewhat. An image of the lamp filament was focused on the slit, *S'*, and the light was concentrated as much as possible on the ground glass in front of slit *S*. The specimen was placed directly in front of slit *S'*, and since its transmission was in general small it was necessary to use rotating sectored discs of known transmission in front of slit *S*. For the readings with the specimen removed a sector was placed in front of *S'*. Color screens were used in front of the ocular slit to exclude stray light. The thickness of each specimen was measured roughly by pressing it between a cover glass and a piece of plate glass with a spherometer. No. 2 was 9.6 μ and No. 1, 6.3 μ thick. From the difference in thickness and the measured transmission of each specimen it is possible to compute

the extinction modulus, $n\kappa$, for this substance. The extinction index may be defined as follows:

$$\kappa = \frac{\lambda}{4\pi d} \log_e \frac{J_1}{J_2},$$

where λ is the wave-length in the material and d is the thickness of material through which the light must pass in order that its intensity may change from J_1 to J_2. The extinction modulus is given by:

$$n\kappa = \frac{\lambda_0}{4\pi d} \log_e \frac{J_1}{J_2},$$

where n is the index of refraction and λ_0 is the wave-length in vacuo. The transmissions of the two specimens are shown by Curves A and B, Fig. 7. The points indicated by crosses (+) were obtained by Dr. J. R. Collins with an infra-red spectrophotometer. Curve C, Fig. 7, shows the transmission of the thinner of the two specimens, No. 1, when placed

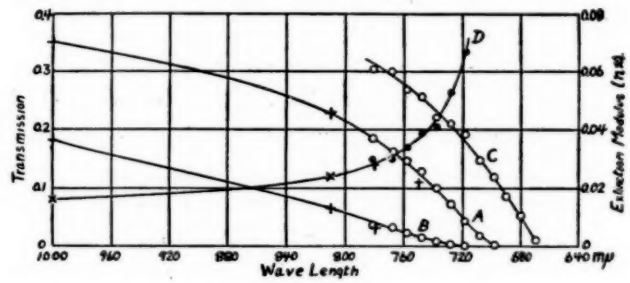


Fig. 7.

Molybdenite: Curve A, transmission of specimen No. 1, 6.3 μ thick; Curve B, transmission of specimen No. 2, 9.6 μ thick; Curve C, transmission of specimen No. 1 placed over liquid air; Curve D, computed extinction modulus, $n\kappa$.

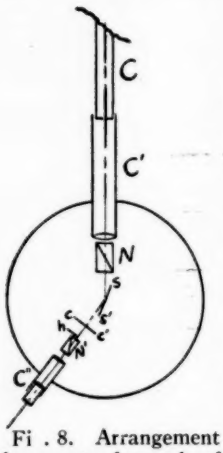
just above liquid air in a Dewar flask. Curve D, Fig. 7, is a plot of the extinction modulus, $n\kappa$, at room temperature, computed from the transmission values as indicated above. The points indicated by $\times$'s were computed from the transmission measurements made by Dr. Collins.

4. Determination of n and κ for Molybdenite and Stibnite.

Plane polarized light is in general converted to elliptically polarized light by reflection at a metallic surface. That this is also the case with absorbing crystals has been shown by Drude [1] theoretically and by Horn,[2] Drude,[3] Müller,[4] and others experimentally. If the elliptic vibration is

[1] Drude, Ann. d. Phys. u. Chem., 32, p. 584, 1887.
[2] Horn, loc. cit.
[3] Drude, Ann. d. Phys. u. Chem., 34, p. 489, 1888.
[4] Müller, loc. cit.

resolved into two components, parallel and perpendicular to the plane of incidence, it is possible to compute the optical constants of the reflecting material in terms of the amplitude ratio and relative phase difference of these two components. For analysis of the elliptically polarized light a Universal Polarimeter was used. This instrument is a modification of the Stokes' analyzer and was devised by Tool.[1] The particular instrument used here is the property of the Bureau of Standards and was very kindly loaned the writer by Dr. C. A. Skinner. It differed from the instrument described by Tool only in having the rotation of the half-shade system read on a fixed circle, instead of relative to the compensator. The set-up is shown diagrammatically in Fig. 8. C is the collimator of a Hilger constant deviation spectroscope used as a monochromator. In train with this instrument was placed a large spectrometer in front of whose collimating lens was a nicol prism, N. This nicol was adjusted by M'Connel's[2] method so that the incident light vector (electric) made an angle of 135°, counterclockwise, with the incident plane for an observer looking towards the source. The specimen, ss', was mounted over the center of the prism table. The polarimeter was mounted on the other arm of the spectrometer. cc' is the mica compensator; h, the mica half-shade; and N', the split nicol. The observing telescope, C'', could be focused either on the half-shade and nicol dividing lines or else on the image of the first slit on the monochromator. The positions of the compensator and half-shade could be read on two attached circles. Only two complementary[3] settings out of the four possible settings of the compensator were used. These two compensator readings are denoted by C' and C, and the corresponding half-shade settings by N' and N. c and n are defined from the following: $C' - C = c$ and $N' - N = c - n$. To obtain the effective order of the half-shade, observations were made with plane polarized light, collimator C' and telescope C'' being in line. Tuckerman[4] has shown that in this case:



Fi . 8. Arrangement of apparatus for study of elliptically polarized light reflected from a crystal surface.

$$\tan 2\eta = \frac{\sin (n - c) \sin (n + c)}{\sin c},$$

[1] Tool, PHYS. REV. (1), 31, p. 1, 1910. Tuckerman, Univ. Neb. Studies (9), pp. 194–203, 1909.

[2] M'Connel, Phil. Mag. (5), 19, p.317, 1885.

[3] Tool, loc. cit., footnote, p. 11.

[4] Tuckerman, loc. cit., p. 198, equ. (76).

where 2η is the average effective order of the half-shade. This varied from 1° 10′ at 680 mμ to 1° 35′ at 490 mμ. The method is rather inaccurate but serves well enough since only cos 2η enters into the computation of the elliptic vibration to be analyzed. From this calibration the average sums of the N readings and of the C readings with plane polarized light were also obtained. These quantities, $N_p' + N_p$ and $C_p' + C_p$, were required later to determine γ, the azimuth with respect to the incident vibration of the major axis of the elliptic vibration.

The method of computing the amplitude ratio and phase difference from the polarimeter readings may be understood by referring to Fig. 9. The x and y axes are chosen in and perpendicular to the plane of incidence, respectively, and perpendicular to the direction of propagation of the light, the positive x axis being horizontal and towards the observer's right. The ellipse to be analyzed has major axis $2a$ and minor axis $2b$, the former making an angle, γ, with the incident vibration,[1] OD (electric vector), and an angle, α, with the incident plane. B is the amplitude of the component y vibration and A of the x vibration. ω is defined as $\tan^{-1} b/a$ and θ' is defined as $\tan^{-1} B/A$. δ is the relative phase difference between the x and y components. Then the following relations hold true:

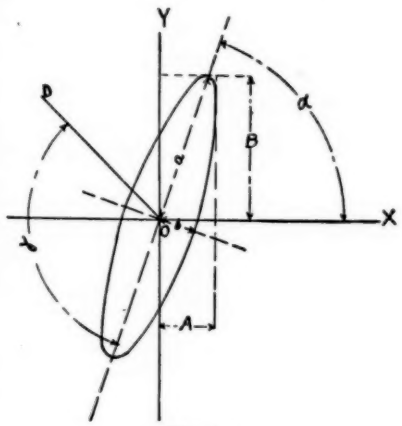


Fig. 9.
Typical elliptic vibration.

$$2\gamma = (N' + N) - (N_p' + N_p) = (C' + C) - (C_p' + C_p),^2$$

$$2\alpha = 2\gamma - 90°,^2$$

$$\cos 2\omega = \frac{\sin n}{\sin c} \cos 2\eta.^3$$

[1] γ is really the angle between the major axis of the ellipse and the electric vector of a plane polarized vibration which would give the same N and C readings with the polarimeter in position for observations on the crystal that were given when the polarimeter was in line with the collimator, the observations actually being made on the incident vibration.

[2] Tool, loc. cit., p. 11.

[3] This formula, which is more exact than the infinite series for determining the ellipticity given by Tuckerman (loc. cit., equations 82 and 83, p. 201), has been deduced by him since the publication of the above. The writer believes that this deduction has not been published yet. The formula was given the writer by Dr. Tool.

$$\cos 2\theta' = \cos 2\omega \cos 2\alpha,^{1}$$

$$\sin \delta = \pm \frac{\sin 2\omega}{\sin 2\theta'}.^{2}$$

To show more fully the method of computation a sample computation is given in Table I.

TABLE I.

Typical Computation to Obtain Amplitude Ratio and Relative Phase Difference.
Molybdenite. $\lambda = 589.3$ mμ. Angle of Incidence = 76°.

Constants.	Polarimeter Readings.
$\log \cos 2\eta = 9.99987$	$N' = 283.23°$
$N_p' + N_p = 297.31°$	$N = 270.36°$
$C_p' + C_p = 195.21°$	$C' = 89.50°$
	$C = 362.08°$

Whence:

$$2\gamma = N' + N - (N_p' + N_p) = 553.59 - 297.31 = 256.28$$
$$2\gamma = C' + C - (C_p' + C_p) = 451.58 - 195.21 = 256.37$$
$$\text{Average,} \quad 256.32°$$

$$2\alpha = 2\gamma - 90° = 166.32 = 166° 19'$$
$$N' - N = c - n = 12.87°$$
$$C' - C = c = -272.58°$$
$$n = -285.43°$$

$$\frac{\sin n}{\sin c} \cos 2\eta = \cos 2\omega \qquad 2\omega = 15° 18'$$

$$\tan \theta' = \frac{B}{A} \qquad \cos 2\theta' = \cos 2\omega \cos 2\alpha$$

$$\cos 2\theta' = \cos (15° 18') \cos (166° 19')$$
$$\cos 2\theta' = -\cos (20° 25')$$
$$2\theta' = 159° 35'$$
$$2\theta = 180° - 2\theta' = 20° 25'$$
$$\tan \theta = \rho = 0.180$$

$$\sin \delta = +\frac{\sin 2\omega}{\sin 2\theta'} = \frac{\sin 15° 18'}{\sin 159° 35'}$$

Therefore

$$\delta = 49° 9'$$
$$\Delta = \pi - \delta = \pi - (49° 9').$$

Both Drude and Müller[3] have given in full detail the necessary formulæ for computing the optical constants of absorbing, rhombic crystals from the amplitude ratio and phase difference of the two component vibrations

[1] Müller u. Pouillet, Lehrb. d. Phys., II., p. 887, equ. 10.

[2] Müller u. Pouillet, Lehrb. d. Phys., II., p. 887, equ. 9.

[3] The general relations for absorbing crystals are developed by Drude (Ann. d. Phys. u. Chem., 32, p. 584, 1887) and applied to stibnite specifically (Ann. d. Phys. u. Chem., 34, p. 489, 1888). Müller gives (loc. cit.) a good summary of Drude's methods and results.

in and perpendicular to the plane of incidence, respectively. These will be summarized here. Referring again to Fig. 9,

$$A/B = \rho = \tan\theta, \qquad \text{where} \qquad \theta = \frac{\pi}{2} - \theta'.$$

Let $\Delta = \pi - \delta$.[1] Then $r = \rho e^{i\Delta}$, where $i = \sqrt{-1}$.

$$R = \frac{1 + r}{1 - r} = x + iy.$$

Then

$$x = \frac{\cos 2\theta}{1 - \sin 2\theta \cos\Delta} \qquad \text{and} \qquad y = \frac{\sin 2\theta \sin\Delta}{1 - \sin 2\theta \cos\Delta}.$$

Drude's theory introduces three complex constants, α, β, and γ, in the direction of the vertical, brachy, and macro axes, respectively. These three constants may be interpreted on the basis of the electromagnetic theory as follows:[2]

$$\alpha = \frac{c^2}{\eta_1}, \qquad \beta = \frac{c^2}{\eta_2}, \qquad \text{and} \qquad \gamma = \frac{c^2}{\eta_3},$$

c being the velocity of light in vacuo and η_1, η_2, η_3 being three complex constants analogous to the three principal dielectric constants in transparent crystals. For stibnite the three constants α, β and γ are different. As Drude has shown, α and β may be found to a first approximation if two sets of observations are made on the crystal, (1) with the vertical axis perpendicular to the plane of incidence and the brachy axis parallel to the plane of incidence, (2) with the vertical axis parallel to the plane of incidence and the brachy axis perpendicular to the plane of incidence. The macro axis is perpendicular to the plane of incidence in each case, since it is perpendicular to the cleavage surface. For these two positions the above quantities are given the subscripts 1 and 2, respectively. If φ is the angle of incidence we have:

$$R_1 + R_2 = (\sqrt{\alpha} + \sqrt{\beta})\frac{\sin^2\varphi}{\cos\varphi}$$

and

$$R_1 - R_2 = (\sqrt{\beta} - \sqrt{\alpha})\frac{1 + \cos^2\varphi}{\cos\varphi}.$$

If we set

$$\sqrt{\alpha} + \sqrt{\beta} = A + iB = \frac{\cos\varphi}{\sin^2\varphi}[(x_1 + x_2) + i(y_1 + y_2)]$$

[1] Drude's formulæ are developed for an incident vibration of azimuth 45°. To develop the results by means of his formulæ it is necessary to use $\Delta = \pi - \delta$. Müller also does this for his results where the azimuth of the incident vibration was not 45°.

[2] Winkelmann, Handb. d. Phys., Vol. 6, p. 1286, or Drude, Theory of Optics (tr. by Mann and Millikan), p. 369, equ. 31, where $a_0^2 = \alpha$, $b_0^2 = \beta$, $c_0^2 = \gamma$.

and

$$\sqrt{\beta} - \sqrt{\alpha} = C + iD = \frac{\cos\varphi}{1 + \cos^2\varphi}[(x_1 - x_2) + i(y_1 - y_2)],$$

then

$$\beta = b + ib' = \frac{(A + C)^2 - (B + D)^2}{4} + \tfrac{1}{2}i(A + C)(B + D),$$

$$\alpha = a + ia' = \frac{(A - C)^2 - (B - D)^2}{4} + \tfrac{1}{2}i(A - C)(B - D).$$

Light incident perpendicularly on the cleavage surface is broken into two waves, traveling in the direction of the macro axis in the crystal, the waves being plane polarized with their planes of polarization mutually perpendicular. Associated with each of these waves is an index of refraction and extinction index. n_1 and κ_1 are obtained from α and n_2 and κ_2 from β, either Drude's or Müller's formulæ being applicable, though the latter are somewhat more convenient for computation. Müller defines angles χ and ϵ such that

$$\tan\chi = \frac{a'}{a} \qquad \text{and} \qquad \tan\epsilon = \frac{b'}{b}.$$

Then

$$\kappa_1 = \tan\frac{\chi}{2} \qquad \text{and} \qquad \kappa_2 = \tan\frac{\epsilon}{2},$$

$$n_1^2 = \frac{\sin 2\frac{\chi}{2}\cos^3\frac{\chi}{2}}{a'} \qquad \text{and} \qquad n_2^2 = \frac{2\sin\frac{\epsilon}{2}\cos^3\frac{\epsilon}{2}}{b'}.$$

For molybdenite α and β were assumed equal [1] since the crystal axes in the cleavage plane are of the same length for this mineral. Only one value of the extinction index and index of refraction is found for molybdenite, namely, that corresponding to light propagated in the direction of the optic axis (*i.e.*, normal to the cleavage plane).

Stibnite.—The results of the observations on this mineral are shown in Table II. and by the curves in Fig. 10. The observations were made on a fresh cleavage surface for each of the two positions of the crystal, the last readings being taken not more than two hours after the crystal was split. Drude and Müller have both investigated the effect of a surface film which forms soon after the surface is exposed to air. Müller concludes that observations taken in the course of a day would be sufficiently accurate for computing the optical constants. In the table,

[1] This is the case of a uniaxial crystal, the reflecting surface being perpendicular to the optic axis. See case I, Drude, Ann. d. Phys., 32, p. 618.

TABLE II.

Stibnite, Angle of Incidence = 74°.

Wave-length.	$\alpha = a + ia'$.		$\beta = b + ib'$.	
	a.	a'.	b.	b'.
680 mμ.....	.0455	.00346	.0463	.00750
670	.0450	.00375	.0457	.00874
650	.0451	.00447	.0433	.0117
630	.0418	.00552	.0442	.0143
610	.0402	.00510	.0438	.0146
589.3	.0366	.00728	.0441	.0144
589.3	.0365	.00867	.0431	.0170
589.3	.0378	.01005	.0433	.0174
570	.0370	.0102	.0423	.0178
550	.0320	.0116	.0386	.0182
530	.0290	.0141	.0376	.0197
510	.0254	.0155	.0336	.0221
490	.0235	.0195	.0308	.0241
480	.0222	.0218	.0252	.0236

By E. C. Müller.

	a_{11}.	a_{12}.	a_{21}.	a_{22}.
656	.0451	.0049	.0480	.0117
610	.0409	.0086	.0501	.0183
589	.0365	.0092	.0472	.0183
527	.0285	.0141	.0406	.0218
510	.0253	.0170	.0386	.0241
486	.0202	.0195	.0350	.0273
460	.0164	.0242	.0312	.0310
434	.0116	.0295	.0274	.0348

however, one may note three sets of readings taken at wave-length 589.3 mμ. These were taken at the beginning, middle, and end of the determinations, respectively. While the values of neither of the indices of refraction are much affected by the changes in α and β, there is considerable change in the extinction indices. Only by using a fresh cleavage surface for each wave-length setting could this difficulty be obviated, and there was not available enough material to make this practicable. In Table II., also, Müller's values of α and β are quoted for comparison. The values of the indices of refraction and extinction indices are plotted in Fig. 10, Müller's points being shown by solid circles (●) and crossed circles (⊕). The agreement on the whole is good. The reflectivity of a substance may be computed from the usual formula

$$R = \frac{(n-1)^2 + \overline{n\kappa^2}}{(n+1)^2 + \overline{n\kappa^2}}.$$

This was done separately for the two values of n and κ. The mean of the two computed reflectivities should be the reflectivity for natural light. These mean values of the reflectivity at perpendicular incidence are plotted in Fig. 3, Curve C, for comparison with the directly observed

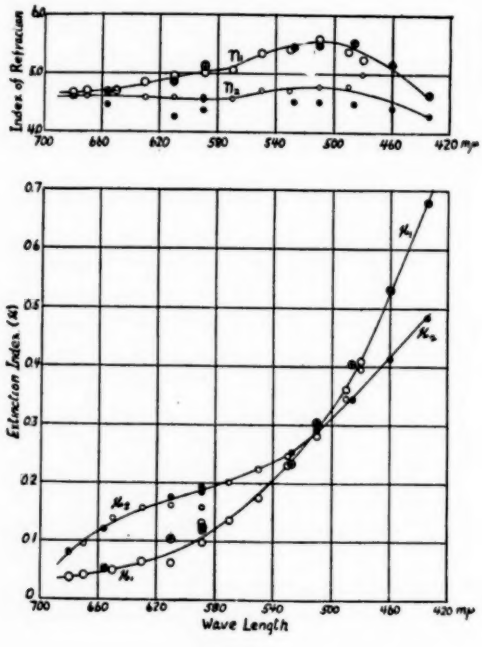


Fig. 10.

Refractive indices and extinction indices for stibnite; ● and ⊕, Müller's values.

reflectivity, values computed from Müller's values of the optical constants being indicated by ×'s.

Molybdenite.—Two determinations were made on molybdenite, one at 70° 10′ incidence and one at 76° incidence. The specimen used throughout was made by splitting one of the samples previously obtained from Dr. Coblentz. It showed no measurable change during the determinations. Some samples of Australian molybdenite obtained from R. M. Wilke, Palo Alto, Calif., on which a few readings were taken, seemed to have a somewhat higher extinction index but practically the same index of refraction. The molybdenite surface obtained by cleavage is not plane and the images of the slit seen in the telescope were spread more or less, although the field was quite uniform when the telescope was focused on the dividing lines. This made it rather difficult to set the specimen exactly at some particular angle of incidence. For this reason the specimen was set as well as possible at the desired angle and then left

in position throughout any one determination. The agreement of the results taken at the two different angles of incidence shows that no considerable error could have arisen from this difficulty. The intensity of the light was also reduced considerably by the lack of a plane surface and it was therefore not possible to carry the readings very far towards the ends of the visible spectrum, although an arc light with its image focused on the slit of the monochromator was used as a source.

The results are shown in Table III. and Figs. 11 and 12. Fig. 11 is a

Table III.

Molybdenite.

Wave-length.	$\varphi = 70° 10'$.		$\varphi = 76°$.		Average a.	Average a'.
	a.	a'.	a.	a'.		
680 mμ.....			.0269	.0093	.0269	.0093
670	.0270	.0136	.0273	.0155	.0272	.0145
660	.0311	.0171	.0309	.0184	.0315	.0179
660	.0319	.0178	.0320	.0185		
650	.0344	.0153	.0367	.0160	.0362	.0157
650	.0359	.0160	.0376	.0154		
640	.0353	.0140	.0351	.0145	.0352	.0143
630	.0320	.0132	.0328	.0141	.0324	.01365
620	.0289	.0143	.0306	.0157	.0294	.0152
620	.0294	.0151				
610	.0294	.0192	.0295	.0198	.0294	.01945
600	.0315	.0228	.0310	.0228	.0312	.0228
589.3	.0347	.0210	.0354	.0216	.0356	.0211
589.3	.0348	.0189				
589.3	.0359	.0209	.0362	.0214		
589.3	.0360	.0211				
589.3	.0353	.0211				
589.3	.0352	.0213				
589.3	.0348	.0209				
589.3	.0362	.0210				
580	.0356	.0190	.0356	.0201	.0356	.01955
570	.0346	.0173	.0353	.0194	.03495	.0184
560	.0339	.0178	.0339	.0181	.0339	.0179
550	.0333	.0167	.0330	.0179	.03315	.0173
540	.0318	.0165	.0324	.0175	.0321	.0170
530	.0301	.0164	.0308	.0174	.0305	.0170
530			.0309	.0178		
520	.0285	.0157	.0289	.0176	.0285	.0165
520	.0276	.0153	.0290	.0175		
510	.0267	.0162			.0267	.0162
500	.0230	.0163	.0241	.0170	.0235	.0166
490			.0208	.0181	.0207	.0181

plot of the values of ρ and δ for wave-length 589.3 mμ at different angles of incidence. The principal angle of incidence as read from the curve

is 78.6°. In Table III. are given the values of the constants a and a' from the two determinations already referred to. The readings at 589.3

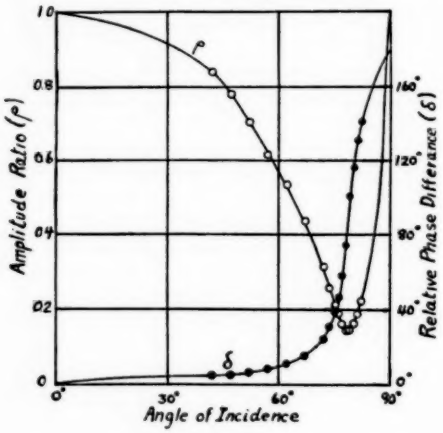


Fig. 11.

Molybdenite: Amplitude ratio (ρ) and phase difference (δ) of the two components of the elliptic vibration for various angles of incidence.

$m\mu$, which were taken at intervals throughout the two determinations, show how little change there is in the surface, quite unlike the change experienced by the stibnite. n and κ are plotted in Fig. 12, while in Fig. 2 the computed reflectivity is plotted (Curve B) for comparison with the observed.

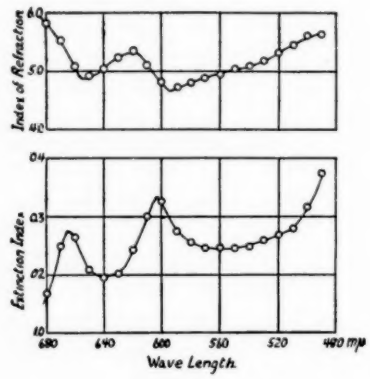


Fig. 12.

Refractive index and extinction index for molybdenite.

5. Discussion of Results.

The reflectivities of the four metallic sulfides are quite similar, being of the same order of magnitude, though the selectivity, on which the surface color depends, differs for pyrite from the other three, each of

which has a maximum in the blue and in the red. The reflection measurements on stibnite and molybdenite reported here are in good agreement, where they overlap with the previous measurements made by Coblentz and Crandall, as reference to their work will show. The values of the extinction indices for stibnite agree well with the values obtained by Drude and Müller. For molybdenite one may compare the directly measured values of the extinction modulus, $n\kappa$, plotted in Fig. 7, with the values obtained by Crandall. At 0.8 μ Crandall gives $n\kappa = 3.9 \times 10^{-4}$ while at 0.81 μ the writer computes 2.4×10^{-2} from the measurements made by Dr. Collins. The difficulty here is probably in the measurement of thickness. Crandall states that two specimens of 4.2 μ and 34 μ thickness, respectively, have identical transmission; and the transmission of either of them (at 1.0 μ) is the same as a specimen 7.0 μ thick reported by Coblentz. The writer's 9.6 μ specimen has a slightly lower transmission (at 1.0 μ) than the three mentioned above, while his 6.3 μ specimen has a lower transmission than a 246 μ specimen also reported by Crandall. There is then no quantitative agreement though the general trend of the curves shows a rapidly decreasing absorption as one goes toward the infra-red. The writer's values of $n\kappa$ obtained by the polarized light measurements unfortunately could not be extended far enough to overlap with the directly measured quantities. The nearest approach is given by $n\kappa = 1.0$ at 680 mμ and $n\kappa = 0.067$ at 718.2 mμ. However, it is just in the region between these two points that the transmission seems to change most rapidly with wave-length.

The indices of refraction of stibnite may be compared with the values obtained by Drude and Müller. The agreement here is especially good for n_1 but not so good for n_2, which is rather hard to understand, since κ_1 and κ_2 agree well and the values of all four of these quantities are computed from the same experimental data. Very little new is brought out about the dispersion and absorption of stibnite that has not been already reported by Müller, though it seemed worth while to get the extra points to fill in his curves. The measurements on stibnite were also of value in testing out the instrument.

The index of refraction and absorption index of molybdenite, so far as the writer knows, have never been obtained before throughout the visible spectrum. In the curve for the latter there are two maxima, at about 600 mμ and 660 mμ. These correspond, as far as one can tell, with the two absorption bands observed by Crandall in a piece of molybdenite 1.0 μ thick. Molybdenite shows anomalous dispersion, the index of refraction having a maximum and two minima in the region measured. The change in the reflectivity at low temperatures is doubtless due

mainly to a change in the index of refraction and only slightly to the change in absorption. The change in the index of refraction at low temperatures has been observed by Trowbridge in the neighborhood of 0.7 μ. However, all of his values, both at room temperature and liquid air temperature, seem too high, agreeing neither with Crandall's computations nor Coblentz's. For instance, he has at 0.7 μ an index of refraction of 11.00. Neglecting the effect of absorption this would give a reflectivity of 70 per cent. at liquid air temperature. No such high reflectivity in molybdenite has been found.

The change in the reflecting power of molybdenite at low temperatures, the writer believes, has not been reported on before. The shift of the bands is toward the shorter wave-lengths, which is the direction of shift for absorption bands and for the photo-conductivity effect.

Molybdenite and stibnite have been compared by various observers to metals in their properties. Possibly in their two most outstanding features, high reflectivity and great opacity, they are alike, but one should notice that the high reflectivity of both these crystals is due rather to a very high index of refraction than to great absorption. Indeed the latter is only of the order of one fourth the absorption for silver.

Coblentz and Kahler have observed the transformation of plane polarized light to elliptically polarized light by reflection at a molybdenite surface, and a stibnite surface using the spectral region 1.0 μ to 4.0 μ. This should of course be true for any absorbing crystal according to Drude's theory. The relation between incident angle and the amplitude ratio and phase difference for the light reflected by molybdenite, as shown by the curves of Fig. 11, is similar to the same quantities observed for stibnite by Drude. Since the reflected light is plane polarized at grazing and perpendicular incidence, the curves for ρ and δ have been completed. Both stibnite and molybdenite produce elliptically polarized light under the conditions used here, in which the light vector rotates clockwise for an observer looking toward the source.

In conclusion the writer wishes to express his thanks to Dr. Coblentz for the mineral samples, to Dr. Skinner for the loan of the instrument and to Dr. Tool for a set of instructions on the use and calibration of the instrument which proved invaluable. Acknowledgment is also made to Professor R. C. Gibbs for aid and helpful suggestions given during the course of the investigation.

CORNELL UNIVERSITY,
September, 1922.

VELOCITY OF SOUND IN SEA WATER.

By E. B. Stephenson.

Abstract.

Velocity of sound in sea water at $-0.3°$ C. over a distance of about 15,500 meters through the waters of Block Island Sound, New York, was found to be 1,453 meters/second, by determining the time for the sound wave produced by the explosion of a bomb to travel to each of five hydrophones anchored at widely separated points, and the distance travelled in each case. The time of detonation was transmitted by radio, and the times of arrival of the wave by cables from the hydrophones to a string galvanometer whose deflections were photographically recorded, together with timing lines at intervals of 1/100 second. The distances were determined by triangulation from two bases on shore. The depth varied from 18 to over 50 meters. The results from the five independent determinations for each of four bombs all lie within ± 0.2 per cent. of the average, indicating that the sound wave had a uniform velocity. It is expected that further studies will enable the effect of variations of temperature, depth, salinity and density on the velocity to be determined.

Object.

THE object of this investigation was to determine the velocity of sound in sea water in a particular locality. The general method consisted in measuring the time required for the sound to travel through the water a known distance of approximately 15,500 meters. The experiments were conducted in January, 1922, in Block Island Sound in the area shown on the map,[1] Fig. 1.

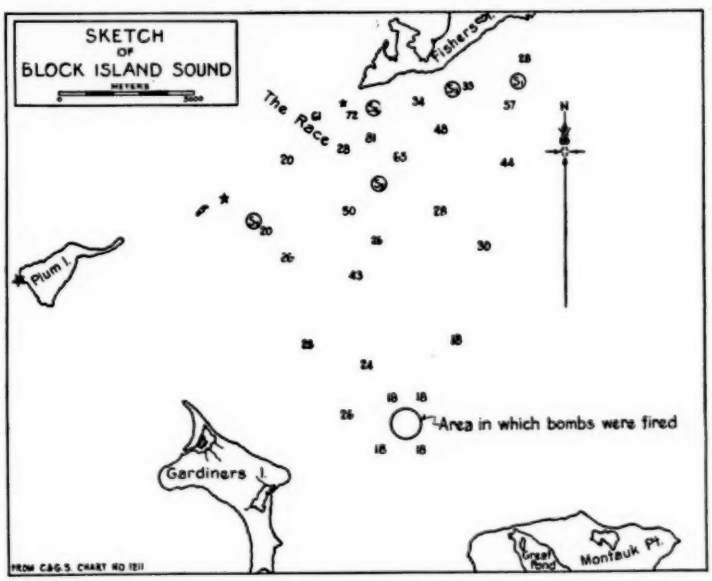


Fig. 1.

[1] Drawn from C. & G. S. Chart 1211. The scattered figures show the depth of the water in meters.

METHOD.

The experimental method consisted in electrically detonating a .5 kg. bomb of TNT at a depth of 8 to 10 meters, and simultaneously sending a radio signal at a distance of approximately 18,000 meters from shore. The sound through the water was received by a series of five hydrophones located as shown in Fig. 1, and connected by cable to a central shore station. The radio signal was received by the usual receiving set and transmitted to the same central station. The schematic apparatus and wiring diagram, Fig. 2, shows the essential elements of the receiving system.[1] A string galvanometer with six strings, a tuning fork con-

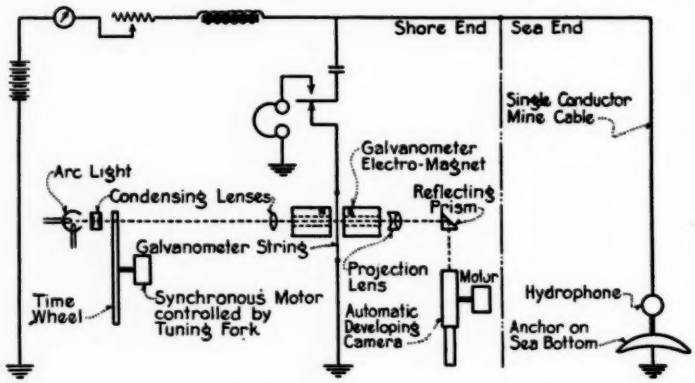


DIAGRAM OF WIRING AND APPARATUS

Fig. 2.

trolled timing device, and a photographic recording camera, gave a record of the vibrations of the strings with transverse timing lines at .01 sec. intervals.

The linear distance between two time lines was equal to 1.1 mm. on the record and the arrival of the sound caused a sharp break in the record of the galvanometer string, so that the time intervals between the explosion of the bomb and the arrival of the sound could be read consistently to .001 sec.

The bombs were suspended from a target float attached by a line to an anchored ship. The location of the bomb at the instant of firing was determined by observations on the target from three shore stations on two base lines about 10,000 meters each in length, and giving intersections of about 40° at the target. Similar observations were made on the

[1] A detailed description of this apparatus is given in a pamphlet by the writer entitled—"Sound Ranging, Occasional Paper No. 63," published by the Engineer School, Camp A. A. Humphreys, Va.

hydrophones at the time of planting, so that the distances from the bomb to each hydrophone could be obtained by computation.

The hydrophones were of four different types, all but one being rigidly attached to 500-kg. anchors about 1 meter from the hard sandy sea bottom in from 20 to 45 meters of water. A single conductor mine cable with grounded return led from each hydrophone to the central station.

The velocity and direction of the tide near the ship from which the bombs were fired was approximately determined, and the temperature was measured by a thermometer suspended from the side of the ship. Studies of these factors are now in progress which are more accurate than the available facilities at that time permitted.

A zero time correction for the radio transmitting and receiving apparatus and for the time of detonation of the bomb was obtained by preliminary trials in the harbor with the same apparatus but using the detonator only at a distance of 6 meters from the receiving hydrophone where any slight error in the assumed velocity of sound in water would be negligible. There was found to be a constant delay of .005 sec. between the transmission of the radio signal and the detonation of the explosive and this correction was subtracted from the observed time interval in each case. This correction was further checked by using a small charge at a distance of 66 meters from the hydrophones, which gave the same correction.

The most serious experimental difficulty was due to the fact that only on rare occasions was there the fortunate favorable coincidence of all the necessary factors. This was particularly true of the visibility, since it was necessary to observe the target simultaneously from three observation stations at distances of approximately 16 kilometers, and to read its angular position to .01°. The effective radio telephone service, which was maintained between the ship and the shore stations, was obviously valuable and in fact almost essential in correlating the observations as well as in giving the time signal.

Four bombs were fired during these experiments and a time record on each bomb was obtained for each of the five hydrophones. The location of each bomb was calculated from two base lines, *A* and *B*, from observations at the three stations, and similarly the distances from each bomb to the hydrophones were computed from the two base lines.

RESULTS.

The data obtained are shown in Table I. No corrections for any factors have been made, except for the time lag of the explosion. The

consistency of the results seems to warrant confidence in the correctness of the theory and general methods. The present knowledge of the direction and velocity of the complicated tidal flow and of the tempera-

TABLE I.

Bomb No.	Hydrophone.	Distance from Bomb to Hydrophone-meters.		Corrected Time Intervals in Seconds.	Velocities in Meters per Second.		Group Averages.
		Base Line *A*.	Base Line *B*.		Base Line *A*.	Base Line *B*.	
1	S_1		15,220.8	10.455		1,455.8	
	S_2	14,211.9	14,202.9	9.775	1,453.9	1,453.0	
	S_3	10,884.1	10,867.9	7.475	1,456.0	1,453.9	1,454.7
	S_4	14,107.5	14,103.0	9.685	1,456.6	1,456.1	
	S_7	11,156.9		7.678	1,453.1		
2	S_1		15,264.6	10.505		1,453.1	
	S_2	14,415.0	14,428.9	9.915	1,453.8	1,455.3	
	S_3	10,894.7	10,892.1	7.502	1,452.2	1,451.9	1,453.4
	S_4	14,117.0	14,115.8	9.711	1,453.7	1,453.5	
	S_7	11,154.5		7.674	1,453.4		
3	S_1		15,243.1	10.487		1,453.5	
	S_2	14,359.9	14,362.5	9.883	1,453.0	1,453.3	
	S_3	10,825.2	10,818.7	7.448	1,453.4	1,452.5	1,453.1
	S_4	14,032.7	14,047.7	9.664	1,452.1	1,453.7	
	S_7	11,042.8		7.599	1,453.2		
4	S_1		15,226.2	10.471		1,454.1	
	S_2	14,334.7	14,337.8	9.861	1,453.7	1,453.9	
	S_3	10,792.8	10,802.7	7.427	1,453.0	1,453.5	1,453.5
	S_4	14,017.2	14,022.4	9.641	1,453.7	1,454.4	
	S_7	10,995.7		7.576	1,451.3		

S_1	Distance 15,240	Average velocity	1,454.1
S_2	" 14,350	" "	1,453.8
S_4	" 14,050	" "	1,454.2
S_3	" 10,850	" "	1,453.3
S_7	" 11,100	" "	1,452.8

Temperature, −.3° C. Average Velocity, 1,453.7.
Salinity 3.35 per cent. Corrected velocity 1,453.3.

ture gradients does not warrant more than approximate corrections, but it is believed that the velocities from bomb No. 1 should be corrected for an effective tide of approximately 1.5 meters per sec., which would make the group average 1,453.2 and the final average 1,453.3 meters per sec. at − .3° C. The salinity was 33.5 parts per thousand.

From a consideration of all the factors, it is believed that the locations of the hydrophone stations are known to within ± 5 m.; locations of the bombs to within ± 10 m.; the time intervals to within ± .001 sec. in 1

sec.; the film readings to within ± .001 sec. in 10 sec., and the average temperature to within ± .2°. The data show the maximum variation in the individual determinations to be ± 3 meters and the group averages to be within ± 1.0 m. in 1,500 m., so that it seems reasonable to believe the final average value is correct to within ± .1 per cent.

It is possible from these same data to calculate the velocity over shorter distances of 1,000 to 5,000 meters, though with less accuracy, from the difference in times of arrival at two hydrophones and the corresponding difference in distance from the bomb. Due to the locations of the hydrophones the velocities for these short distances may be considerably affected by tidal flow, temperature differences, and changes in depth, but there are not yet sufficient data concerning these factors to warrant definite conclusions. However, the average of 36 different, uncorrected, short distance velocities is 1,456.6 meters per sec., and 70 per cent. of the individual determinations are greater than the average of 1,453.3 meters per sec., indicating a slightly greater velocity over these short distances under the conditions obtaining at the time of the experiments.

During July and August, 1921, about 100 separate determinations of the velocity of sound in the water of this area gave an average of 1,486 meters per sec. These data were subject to numerous variable errors that have been eliminated in the present experiments, and the temperatures were only approximate, but the general average checks with the present data within .2 per cent.

These experiments are being continued and more extensive data will be obtained, particularly as to the effects on the velocity of sound, of the depth, temperature and salinity of the water, and of the velocity and direction of the tidal currents. These factors having been determined, a more adequate theory as to the method of propagation of sound waves in water can be developed and accurate numerical corrections can be made. The sound method also has possibilities of wide usefulness in hydrographic work.

The writer wishes to acknowledge his full indebtedness to the Subaqueous Sound Ranging Section of the Coast Artillery Corps at Fort H. G. Wright, New York, particularly, Colonel R. S. Abernethy, Officer in Charge, Major H. C. Allen, Captains E. C. Seeds, J. B. Muir and E. D. Weigle, 1st Lieut. S. Rubin, the non-commissioned staff officers, and the non-commissioned officers and the enlisted personnel of the 132d Co., C. A. C., who so successfully conducted these experiments under difficult conditions.

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APPLICATIONS OF FUNCTIONS WITH MULTIPLICATIVE PERIODS.

By Jakob Kunz.

Abstract.

Potential around a long charged wire between two earthed concentric cylinders.—If the radii are R_1 and R_2 and the radial distance to the wire is p_0, then the radial distances to the first two images of the charge e per unit length are $p_1 = R_1^2/p_0$ and $p_2 = R_2^2/p_0$ and the potential P at any point z is the real part of $2e \log R(z)$ where $R(z) = S_2(z)/S_0(z) = \Pi_1^\infty(1 - p_2m^k/z)\Pi_0^\infty(1 - zm^k/p_2)/\Pi_1^\infty(1 - p_0m^k/z)\Pi_0^\infty(1 - zm^k/p_0)$, in which $m = p_1/p_2 < 1$. The equation for P is then transformed to a singly infinite sum of logarithms.

Properties of functions with multiplicative periods, involving infinite products.—If we put $f(z) = z^{-\beta}R(z)$, where $\beta = 2 \log (R_1/p_0)/\log m$, then $f(mz) = f(z)$. Not only $f(z)$ but z^n times the nth derivative of $f(z)$ is a multiplicative function with period m. The poles and zeros of $f(z)$ are discussed. Also $S_2(mz) = -(p_2/z)S_2(z)$. $S(z)$ can be transformed to a singly-infinite product $G(x) = (1 - e^{iz})\Pi_1^\infty(1 - 2m^k \cos x + m^{2k})$. The relation of this function $G(x)$ to the *function $\sigma(x)$ of Weierstrass* is pointed out. They have the same zeros but the periods are different. The quotient $Q(x) = \sigma(x)/G(x) = e^{(ax^2-x/2)}$. Finally $\sigma(x)$ is expressed as a singly-infinite product.

THE investigation of the following physical problem will lead to functions with multiplicative periods. These functions can be transformed into elliptic functions, for instance, into the σ function of Weierstrass, and a very useful form of that function, which is otherwise not easily accessible, can be obtained in a very simple way. The study of the functions with multiplicative periods opens a very direct access to the theory of elliptic functions.

We consider in Fig. 1 two long coaxial cylinders of radii R_1 and R_2.

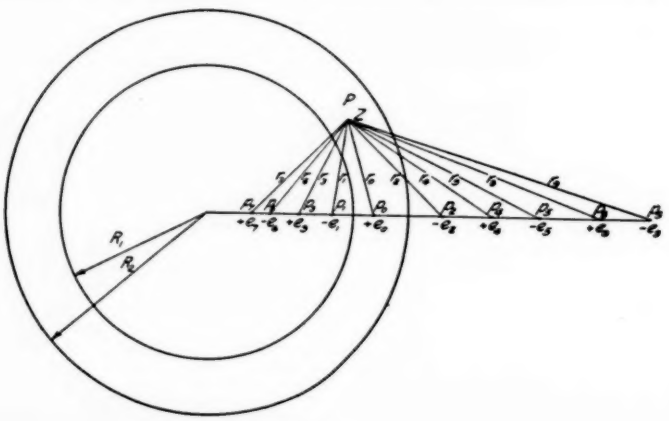

Fig. 1.

A wire is stretched parallel to these cylinders, passing through a point, whose distance from the center O is p_0. This wire carries the charge e per unit length. The potential of the two cylinders is equal to zero. The potential P shall be determined in any point between the two cylinders. The problem is a two-dimensional one. We consider the images $e_1, e_2, e_3, e_4 \cdots$ of e in the points $p_1, p_2, p_3, p_4 \cdots$. The image charges $e_1, e_2 \cdots$ are given by the equations: $e_1 = -e$; $e_2 = -e$; $e_3 = -e_2 = e$; $e_4 = -e_1 = e$; $e_5 = -e_3 = -e$; $e_6 = -e_4 = -e$, etc. And the distances $p_1, p_2, p_3 \cdots$ from the center are given by:

$$p_0p_1 = R_1^2, \quad p_0p_2 = R_2^2, \quad p_2p_3 = R_1^2, \quad p_1p_4 = R_2^2, \quad p_3p_5 = R_2^2,$$
$$p_4p_6 = R_1^2, \quad p_5p_7 = R_1^2, \quad p_6p_8 = R_2^2, \quad p_7p_9 = R_2^2, \quad p_8p_{10} = R_1^2.$$

The distances between the charges and the point P shall be $r_0, r_1, r_2, r_3, r_4 \cdots$. The complex number corresponding to the point P shall be z, then we can write:

$$r_0 = |z - p_0|, \quad r_1 = |z - p_1|, \quad r_2 = |z - p_2|, \quad r_3 = |z - p_3| \cdots$$

and the potential P appears in the form:

$$P = -2e \log r_0 + 2e \log r_1 + 2e \log r_2 - 2e \log r_3 - 2e \log r_4 + 2e \log r_5 + 2e \log r_6 - 2e \log r_7 - 2e \log r_8 + 2e \log r_9 + \cdots$$

or

$$P = 2e \log \frac{r_1 r_2 r_5 r_6 r_9 r_{10} \cdots}{r_0 r_3 r_4 r_7 r_8 r_{11} r_{12} \cdots}.$$

But $\log r = \log |z| = R_e \log z$, where R_e means "the real part of"; hence

$$P = 2e\, R_e \log \frac{(z - p_1)(z - p_2)(z - p_5)(z - p_6)(z - p_9)(z - p_{10}) \cdots}{(z - p_0)(z - p_3)(z - p_4)(z - p_7)(z - p_8)(z - p_{11}) \cdots},$$

$$P = 2e\, R_e \log \frac{\left(z - \frac{R_1^2}{p_0}\right)\left(z - \frac{R_2^2}{p_0}\right)\left(z - \frac{R_2^4}{R_1^2 p_0}\right)\left(z - \frac{R_1^4}{R_2^2 p_0}\right) \cdots}{(z - p_0)\left(z - \frac{R_1^2}{R_2^2} p_0\right)\left(z - \frac{R_2^2}{R_1^2} p_0\right)\left(z - \frac{R_1^4}{R_2^4} p_0\right) \cdots}.$$

Let

$$m = \left(\frac{R_1}{R_2}\right)^2 < 1, \quad a = \frac{R_1^2}{p_0} = p_1, \quad b = \frac{R_2^2}{p_0} = p_2, \quad m = a/b = p_1/p_2.$$

Then the potential P appears in the form:

$$P = 2e\, R_e \log \frac{(z-a)(z-am)(z-am^2) \cdots (z-b)\left(z - \frac{b}{m}\right)\left(z - \frac{b}{m^2}\right) \cdots}{(z - p_0)(z - p_0 m)(z - p_0 m^2) \cdots \left(z - \frac{p_0}{m}\right)\left(z - \frac{p_0}{m^2}\right) \cdots}.$$

$$P = 2e\ R_e \log \frac{\left(1-\frac{bm}{z}\right)\left(1-\frac{bm^2}{z}\right)\cdots\left(1-\frac{z}{b}\right)\left(1-\frac{zm}{b}\right)\cdots}{\left(1-\frac{p_0}{z}\right)\left(1-\frac{p_0 m}{z}\right)\cdots\left(1-\frac{zm}{p_0}\right)\left(1-\frac{zm^2}{p_0}\right)\cdots}.$$

$$P = 2e\ R_e \log \frac{\prod_{k=1}^{\infty}\left(1-\frac{bm^k}{z}\right)\prod_{k=0}^{\infty}\left(1-\frac{m^k z}{b}\right)}{\prod_{k=0}^{\infty}\left(1-\frac{p_0 m^k}{z}\right)\prod_{k=1}^{\infty}\left(1-\frac{zm^k}{p_0}\right)}. \tag{1}$$

We proceed to consider the function $R(z)$,

$$R(z) = \frac{\prod_{k=1}^{\infty}\left(1-\frac{bm^k}{z}\right)\prod_{k=0}^{\infty}\left(1-\frac{m^k z}{b}\right)}{\prod_{k=0}^{\infty}\left(1-p_0\frac{m^k}{z}\right)\prod_{k=1}^{\infty}\left(1-\frac{zm^k}{p_0}\right)},$$

$$R(mz) = R(z)\frac{\left(1-\frac{b}{z}\right)\left(1-\frac{mz}{p_0}\right)}{\left(1-\frac{z}{b}\right)\left(1-\frac{p_0}{mz}\right)} = R(z)\frac{(z-b)(p_0-mz)}{(b-z)(mz-p_0)}\frac{bm}{p_0},$$

$$R(mz) = R(z)\cdot\frac{a}{p_0} = R(z)\frac{R_1^2}{p_0^2}.$$

We arrive then at the functional equation:

$$R(mz) = R(z)\frac{R_1^2}{p_0^2}.$$

A particular solution can be found by: $R(z) = z^\beta$, then

$$R(mz) = m^\beta z^\beta = z^\beta\ R_1^2/p_0^2 \text{ or } m^\beta = R_1^2/p_0^2 \text{ or } \beta = 2\frac{\log R_1/p_0}{\log m}.$$

We may now write:

$$R(z) = \frac{\prod_{k=1}^{\infty}\left(1-\frac{bm^k}{z}\right)\prod_{k=0}^{\infty}\left(1-\frac{m^k z}{b}\right)}{\prod_{k=0}^{\infty}\left(1-\frac{p_0 m^k}{z}\right)\prod_{k=1}^{\infty}\left(1-\frac{m^k z}{p_0}\right)} z^\beta \cdot z^{-\beta}.$$

In this way we arrive at a function $f(z)$ with a multiplicative period:

$$f(z) = \frac{\prod_{k=1}^{\infty}\left(1-\frac{bm^k}{z}\right)\prod_{k=0}^{\infty}\left(1-\frac{m^k z}{b}\right)}{\prod_{k=0}^{\infty}\left(1-\frac{p_0 m^k}{z}\right)\prod_{k=1}^{\infty}\left(1-\frac{m^k z}{p_0}\right)} \cdot z^{-\beta},$$

so that $f(mz) = f(z)$ where m is smaller than 1.

We shall next consider a few properties of such functions. By differentiation of this equation we obtain: $mf'(mz) = f'(z)$; *i.e.*, the derivative has not the multiplicative period m of the original function. Let us introduce a new function: $f_1(z) = zf'(z)$, then we get $f_1(mz) = mz \cdot f'(mz) = zf'(z) = f_1(z)$, or the function $f_1(z) = zf'(z)$ has a multiplicative period m, also the function $zf'(z) - f(z)$; differentiating this function we obtain $zf''(z)$ which is non-periodic. If we multiply this function with z we obtain again a periodic function $z^2f''(z)$. In the same way it can be shown that $z^nf^{(n)}(z)$ is a function with a multiplicative period m.

The function $f(z)$ has zeros and poles and an essential singularity at $z = 0$, otherwise it is an analytic function. We consider a circular ring in the z plane bounded by two concentric circles C_1 and C_2 whose radii are r for the outer circle C_2 and mr for the inner circle C_1. Around this closed region we take the integral

$$\int \frac{f(z)}{z} dz = \int_{C_2} \frac{fz}{z} dz - \int_{C_1} \frac{f(z)}{z} dz.$$

On the circle C_2 we have $z = re^{i\vartheta}$; $dz = rie^{i\vartheta}d\vartheta = izdd\vartheta$. On the inner circle C_1 we have: $z = mre^{i\vartheta}$; $dz = izd^{\vartheta}$. Hence the integral

$$T = \int \frac{f(z)}{z} dz = \int_0^{2\pi} f(re^{i\vartheta})id\vartheta - \int_0^{2\pi} f(re^{i\vartheta})id\vartheta = 0.$$

But the sum of the residues in the ring considered is equal to

$$\frac{1}{2\pi i} \int \frac{f(z)}{z} dz$$

or equal to zero; therefore our function $f(z)/z$ cannot have a single pole of the first order in the ring, it must have at least either two poles of the first order or one pole of the second order.

In the next place let us consider the integral of the logarithmic derivative around the fundamental ring whose boundary contains no zeros or poles.

$$\int \frac{f'(z)}{f(z)} dz = \int \frac{1}{z} \left[\frac{zf'(z)}{f(z)} \right] dz = 0,$$

since both numerator and denominator of the bracket have the same multiplicative period; the integral is therefore of the type considered before and vanishes. But this integral, multiplied by $1/2\pi i$, is equal to the difference of the number of zeros and poles of $f(z)$ within the annular region. The number of poles is therefore equal to the number of zeros.

We consider the functions

$$S(z) = \prod_{k=1}^{\infty} \left(1 - \frac{bm^k}{z} \right) \prod_{k=0}^{\infty} \left(1 - \frac{m^k z}{b} \right) = P_2(z)P_1(z)$$

where

$$P_1(z) = \left(1 - \frac{z}{b}\right)\left(1 - \frac{mz}{b}\right)\left(1 - \frac{m^2z}{b}\right)\cdots = \prod_{k=0}^{\infty}\left(1 - \frac{m^kz}{b}\right)$$

and

$$P_2(z) = \left(1 - \frac{bm}{z}\right)\left(1 - \frac{bm^2}{z}\right)\left(1 - \frac{bm^3}{z}\right)\cdots = \prod_{k=0}^{\infty}\left(1 - \frac{bm^k}{z}\right);$$

then we find

$$P_2(mz) = \left(1 - \frac{b}{z}\right)P_2(z) \text{ and } P_1(mz) = P_1(z)\frac{1}{1 - z/b}$$

and

$$P_2(mz)P_1(mz) = -\frac{b}{z}P_1(z)P_2(z), \qquad \text{or} \qquad S(mz) = -\frac{b}{z}S(z)$$

and we see that we can build up functions with multiplicative periods by means of such functions $S(z)$.

In

$$S(z) = \left(1 - \frac{z}{b}\right)\prod_{k=1}^{\infty}\left[1 - 2m^k\left(\frac{b}{z} + \frac{z}{b}\right)\frac{1}{2} + m^{2k}\right]$$

we substitute $z = be^{ix}$ and obtain

$$Sz = G(x) = (1 - e^{ix})\prod_{k=1}^{\infty}(1 - 2m^k\cos x + m^{2k}).$$

Returning to equation (1) we obtain

$$Re\log\left(1 - \frac{z}{b}\right)\prod_{k=1}^{\infty}\left[1 - 2m^k\left(\frac{b}{z} + \frac{z}{b}\right)\frac{1}{2} + m^{2k}\right] \tag{2}$$

$$= Re\log(1 - e^{ix}) + Re\sum_{k=1}^{\infty}\log(1 - 2m^k\cos x + m^{2k});$$

x itself is now the complex variable, equal to $u + iv$;

$$\cos(u + iv) = \cos u\cos hv - i\sin u\sin hv.$$

$$\begin{aligned}
&Re\log(1 - 2m^k\cos(u + iv) + m^{2k}) \\
&\quad = Re\log[1 + m^{2k} - 2m^k\cos u\cos hv + i2m^k\sin u\sin hv] \\
&\quad = Re\log(X + iY) = \tfrac{1}{2}\log(X^2 + Y^2) \\
&\quad = \tfrac{1}{2}\log[(1 + m^{2k} - 2m^k\cos u\cos hv)^2 + (2m^k\sin u\sin hv)^2] \\
&\quad = \tfrac{1}{2}\log[1 + 2m^{2k} + m^{4k} - 4m^k\cos u\cos hv(1 + m^{2k}) \\
&\qquad\qquad + 4m^{2k}(\cos^2 u + \sin^2 hv)].
\end{aligned}$$

$$\begin{aligned}
Re\log(1 - e^{iz}) &= Re\log[1 - e^{i(u+iv)}] = Re\log[1 - e^{iu}e^{-v}] \\
&= Re\log[1 - (\cos u + i\sin u)e^{-v}] \\
&= Re\log[1 - e^{-v}\cos u - i\sin ue^{-v}] \\
&= \tfrac{1}{2}\log(1 - 2e^{-v}\cos u + e^{-2v}).
\end{aligned}$$

Equation (2) assumes now the following form:

$$Re \log\left(1 - \frac{z}{b}\right)\prod_{k=1}^{\infty}\left[1 - 2m^k\left(\frac{b}{z}+\frac{z}{b}\right)\frac{1}{2} + m^{2k}\right]$$
$$= \tfrac{1}{2}\log(1 - 2e^{-v}\cos u + e^{-2v}) + \tfrac{1}{2}\sum_{k=1}^{\infty}[1 + 2m^{2k} + m^{4k} \qquad (3)$$
$$- 4m^k \cos u \cos hv(1 + m^{2k}) + 4m^{2k}(\cos^2 u + \sin^2 hv)].$$

If $\mathfrak{p}$ and $\mathfrak{y}$ are the coördinates of P, *i.e.*, if $z = \mathfrak{p} + i\mathfrak{y} = \mathfrak{r}e^{i\vartheta}$, then we have the following substitutions:

$$z = \mathfrak{p} + i\mathfrak{y} = be^{iz} = be^{i(u+iv)} = be^{-v}e^{iu}, \qquad \mathfrak{p} = be^{-v}\cos u,$$
$$\mathfrak{y} = be^{-v}\sin u, \qquad \mathfrak{r} = be^{-v}, \qquad u = \vartheta,$$
$$\cos hv = \frac{1}{2}\left[\frac{b}{\mathfrak{r}} + \frac{\mathfrak{r}}{b}\right], \qquad \sin hv = \frac{1}{2}\left[\frac{b}{\mathfrak{r}} - \frac{\mathfrak{r}}{b}\right].$$

We have so far transformed the numerator under the logarithm of equation (1). We can treat the denominator in exactly the same way and write:

$$\prod_{k=0}^{\infty}\left(1 - \frac{p_0 m^k}{z}\right)\prod_{k=1}^{\infty}\left(1 - \frac{zm^k}{p_0}\right)$$
$$= \left(1 - \frac{p_0}{z}\right)\prod_{k=1}^{\infty}\left[1 - 2m^k\left(\frac{p_0}{z}+\frac{z}{p^0}\right)\frac{1}{2} + m^{2k}\right].$$

Substituting $z = p_0 e^{i\bar{z}}$ and $\bar{x} = \bar{u} + i\bar{v}$, we obtain as before:

$$Re \log\left(1 - \frac{p_0}{z}\right)\prod_{k=1}^{\infty}\left[1 - 2m^k\left(\frac{p_0}{z}+\frac{z}{p_0}\right)\frac{1}{2} + m^{2k}\right]$$
$$= \tfrac{1}{2}\log(1 - 2e^{v}\cos\bar{u} + e^{2\bar{v}}) + \tfrac{1}{2}\sum_{k=1}^{\infty}\log[1 + 2m^{2k} + m^{4k} \qquad (4)$$
$$- 4m^k \cos\bar{u}\cos h\bar{v}(1 + m^{2k}) + 4m^{2k}(\cos^2\bar{u} + \sin^2 h\bar{v})]$$

where

$$z = \mathfrak{p} + i\mathfrak{y} = \mathfrak{r}e^{i\vartheta} = p_0 e^{i(\bar{u}+i\bar{v})} = p_0 e^{-\bar{v}+i\bar{u}} = p_0 e^{-\bar{v}}(\cos\bar{u} + i\sin\bar{u}),$$
$$\mathfrak{r} = p_0 e^{-\bar{v}}, \qquad \vartheta = \bar{u}.$$

Combining the equations (1), (3) and (4) we obtain the final result in the following form:

$$P = 2e\left\{\log\frac{1 - 2e^{-v}\cos u + e^{-2v}}{1 - 2e^{\bar{v}}\cos\bar{u} + e^{2\bar{v}}}\right.$$
$$+ \prod_{k=1}^{\infty}\log[1 + 2m^{2k} + m^{4k} - 4m^k\cos u\cos hv(1 + m^{2k})$$
$$+ 4m^{2k}(\cos^2 u + \sin^2 hv)] \qquad (5)$$
$$\left. - \prod_{k=1}^{\infty}\log[1 + 2m^{2k} + m^{4k} - 4m^k\cos\bar{u}\cos h\bar{v}(1 + m^{2k})\right.$$
$$\left. + 4m^{2k}(\cos^2\bar{u} + \sin^2 h\bar{v})]\right\}.$$

In the next section we shall point out the relation between the function

$$S(z) = G(x) = (1 - e^{ix}) \prod_{k=1}^{\infty} (1 - 2m^k \cos x + m^{2k})$$

and the function $\sigma(x)$ of Weierstrass. The zeros of the function

$$S(z) = \left(1 - \frac{z}{b}\right) \prod_{k=1}^{\infty} \left(1 - \frac{m^k b}{z}\right) \prod_{k=1}^{\infty} \left(1 - \frac{m^k z}{b}\right)$$

are given by the values of $z = m^{l_1} \cdot b$, where l_1 is an integer between $-\infty$ and $+\infty$. We shall put $\log m/2\omega_1 = i = \sqrt{-1}$, then the zeros of $G(x)$ are given by the values of x determined by the equation:

$$bm^{l_1} = z = be^{ix} = be^{x \frac{\log m}{2\omega_1}}$$

or

$$m^{l_1} = e^{\left(x \frac{\log m}{2\omega_1} \pm 2\pi i l_2\right)}$$

or

$$l_1 \log m = x \frac{\log m}{2\omega_1} \pm 2\pi i l_2$$

or

$$x = l_1 2\omega_1 + \frac{2\pi i l_2}{i} = l_1 2\omega_1 + l_2 2\omega_2$$

where $l_2 = -\infty \cdots +\infty$ and where we have put $\omega_2 = \pi$. If we choose therefore $\omega_2 = \pi$ and $\omega_1 = (\log m)/2i$, then the zeros of $G(x)$ are identical with the zeros of $\sigma(x)$ of Weierstrass. We wish next to find the periodic properties of $G(x)$, after the following transformations:

$$G(x) = (1 - e^{ix}) \prod_{k=1}^{\infty} [1 - m^k(e^{ix} + e^{-ix}) + m^{2k}]$$

$$= (1 - e^{ix}) \prod_{k=1}^{\infty} [1 - 2m^k \cos x + m^{2k}] \frac{(1 - m^k)^2}{(1 - m^k)^2},$$

$$G(x) = e^{\frac{ix}{2}} [e^{-\frac{ix}{2}} - e^{\frac{ix}{2}}] \prod (1 - m^k)^2 \prod_{k=1}^{\infty} \frac{1 - 2m^k \cos x + m^{2k}}{(1 - m^k)^2}.$$

Using the relation $2i \sin x = e^{ix} - e^{-ix}$ and putting $-2i \prod (1 - m^k)^2 = C$, a constant, we get the form

$$G(x) = Ce^{\frac{ix}{2}} \sin \frac{x}{2} \prod \frac{1 - 2m^k \cos x + m^{2k}}{(1 - m^k)^2};$$

hence

$$G(x + 2\omega_2) = G(x + 2\pi) = G(x), \tag{6}$$

or $G(x)$ has the period $2\omega_2$. In order to find the expression $G(x + 2\omega_2)$,

we remember:

$$S(mz) = -\frac{b}{z}S(z).$$

If we put $z = be^{ix}$, then

$$mz = mbe^{ix} = be^{i\left(x + \frac{\log m}{i}\right)} = be^{i(x+2\omega_1)}.$$

If z goes over into mz, then x goes over into $(x + 2\omega_1)$, hence

$$G(x + 2\omega_1) = \left(-\frac{b}{z}S(z)\right) = -e^{-ix}G(x). \tag{7}$$

With the equations (6) and (7) we compare the corresponding functional equations of $\sigma(x)$:

$$\begin{aligned} \sigma(x + 2\omega_2) &= -e^{2\eta_1(x+\omega_1)}\sigma(x), \\ \sigma(x + 2\omega_1) &= -e^{2\eta_2(x+\omega_2)}\sigma(x), \end{aligned} \tag{8}$$

where $\eta_1\omega_2 - \eta_2\omega_1 = \pm \frac{1}{2}\pi i$. $G(x)$ and $\sigma(x)$ have the same zeros, but the periodicities are different. We consider now the quotient $Q(x)$ of the two functions $\sigma(x)$ and $G(x)$,

$$Q(x) = \frac{\sigma(x)}{G(x)}.$$

This quotient has no zeros and poles in the finite plane.

$$Q(x + 2\omega_1) = \frac{\sigma(x + 2\omega_1)}{G(x + 2\omega_1)} = e^{2\eta_1(x+\omega_1)+ix} \cdot Q(x), \tag{9}$$

$$Q(x + 2\omega_2) = \frac{\sigma(x + 2\omega_2)}{G(x + 2\omega_2)} = -e^{2\eta_2(x+\omega_2)}Q(x) = e^{2\eta_2(x+\omega_2)-\Pi i}Q(x). \tag{10}$$

We assume a solution of the form: $Q(x) = e^{ax^2+bx}$. Substituting in both equations, we find $b = -i/2$ and $a = \eta_2/2\pi$ if we, in accordance with the periods $2\omega_1$ and $2\omega_2$, choose the negative sign in the equation: $\eta_1\omega_2 - \eta_2\omega_1 = \pm \frac{1}{2}\pi i$. The function

$$\frac{Q(x)}{e^{\left[\frac{\eta_2}{2\pi}x^2 - \frac{i}{2}x\right]}}$$

has no zeros and poles in the finite plane, and is doubly periodic, it is therefore a constant $(= 1)$;

$$Q(x) = \frac{\sigma(x)}{G(x)} = e^{\frac{\eta_2}{2\pi}x^2 - \frac{i}{2}x} \cdot C.$$

$$\sigma(x) = Ce^{\frac{\eta_2}{2\pi}x^2 - \frac{i}{2}x}G(x), \tag{11}$$

$$\sigma(x) = Ce^{\frac{\eta_2}{2\pi}x^2} \sin\frac{x}{2}\prod_{k=1}^{\infty}\frac{1 - 2m^k\cos x + m^{2k}}{(1 - m^k)^2}.$$

By definition we have

$$\lim_{x=0} \frac{\sigma(x)}{x} = 1,$$

hence:

$$\sigma(x) = 2e^{\frac{\eta_2}{2\pi} x^2} \sin\frac{x}{2} \prod_{k=1}^{\infty} \frac{1 - 2m^k \cos x + m^{2k}}{(1 - m^k)^2}.$$

I am very much obliged to Professor R. D. Carmichael for several important suggestions.

UNIVERSITY OF ILLINOIS,
September 18, 1922.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE CHICAGO MEETING, DECEMBER 1 AND 2, 1922.

THE 117th regular meeting of the Society was held at the University of Chicago on Friday and Saturday, December 1 and 2, 1922. There were morning and afternoon sessions on both days with an attendance of about one hundred and forty members and visitors. The presiding officer was Professor Theodore Lyman, President of the Society.

The meeting of the Council on the evening of Friday, December 1, 1922, at the Quadrangle Club, was attended by eleven members. There was an extended discussion of the methods of conducting the business of the Society with regard to the offices of the Secretary, Treasurer and Managing Editor. A report was received from the Educational Committee. Seventy-nine persons were *elected to membership* in the Society, as follows: John G. Albright, Elda E. Anderson, Lester Aronberg, Evelyn Aylesworth, Bentley Barnes, Richard Bell, C. Ray Bender, Robert H. Berryhill, Björnson Björns, Earl R. Bordner, Joseph C. Boyce, Francis C. Breckenridge, James E. Brock, Hugh A. Brown, Joseph Thompson Butterfield, A. Courtenay Carson, S. H. Chao, Evelyn Ogden Clift, E. Hobart Collins, A. F. Corby, Jr., Garabed K. Daghlian, Charles S. Demarest, Lee A. DuBridge, H. K. Dunn, Frank M. Durbin, William Godey Ellis, George Gilbert, Burgoyne Griffing, Henry Hartig, Julia F. Herrick, Horace VanNorman Hilberry, Barton Hoag, Paul C. Hoernel, W. J. Hooper, F. L. Hopper, Thomas Ellwood Huff, R. O. Hutchinson, Axel Georg Jensen, Reginald L. Jones, O. E. Koepp, Karl Gottfrid Larson, Logan L. Lauer, Thomas L. Lee, S. W. Leifsen, V. P. Lubovich, John Joseph Lynch, Herbert P. McNally, H. B. Maris, Milton Marshall, Carl W. Miller, L. W. Morris, Peter J. Mulder, Ralph P. Newhall, Zeus Rud Nielsen, G. B. Obear, William E. Orvis, Newell D. Parker, Kenneth H. Pratt, Isaac Rabinovitz, A. H. Rollefson, H. D. Roop, Cyril Ruhlmann, R. B. Sawyer, Ernst H. Schreiber, Forest Shollemberger, Lloyd Smede, Arthur Bessey Smith, Frederic H. Smyser,

Theodore Soller, Winthrop H. Stanley, R. D. Summers, George E. Thompson, William A. Tripp, C. M. Tuttle, W. W. Watson, B. B. Weatherby, 2d, Lester Wolfe, Paul R. Yoder, Otis B. Young.

A program of fifty-four papers was presented. Abstracts of these papers are given in the following pages. Eight of these, numbered 1, 4, 6, 9, 28, 46, 51 and 52, were read by title only.

DAYTON C. MILLER, *Secretary.*

ABSTRACTS OF PAPERS.

1. The torques and forces between short cylindrical coils carrying undamped alternating currents of radio frequency. W. A. PARLIN, University of Iowa.—Measurements of the torques and forces between two short single layer cylindrical coils carrying undamped currents alternating at radio frequencies showed variations with the frequency of the current oscillation not predicted from the classical formulas of Maxwell and others. When the current in the coils and the angle between the planes of the coils were maintained constant, the torque between the two coils connected in series, with the currents in the same sense, was found to remain approximately constant as the frequency of the current increased from 60 to 0.3×10^6 cycles per second, but when the frequency increased from 0.3×10^6 to 1.5×10^6 cycles per second, the torque increased with the frequency, in some cases being more than doubled. The rate of increase of the torque with the frequency decreased to zero as the angle between the planes of the coils increased from 10° to 90°, and remained zero within the error of experiment as the angle changed from 90° to 180°, *i.e.*, when the currents were in the opposite sense.

The forces between the two coils connected in series with their planes parallel showed a similar change with frequency. When the currents in the two coils and also the distance between the coils were maintained constant, and the currents were in the same sense, the force increased, in certain cases to twice its initial value, as the frequency of the current increased from 0.3×10^6 to 1.5×10^6 cycles per second. The rate of increase of force with frequency increased as the distance apart of the coils increased. When the currents in the two coils were in opposite senses no change in force with frequency was observed.

From a consideration of the various phenomena of radio frequency currents not taken into account by the classical theory, it seems that an explanation of the foregoing facts is to be sought in the effect of the energy radiated from the coils in the form of electromagnetic waves.

2. Hall effect and specific resistance of evaporated films of silver, copper, and iron. J. C. STEINBERG, University of Iowa.—The Hall effect and specific resistance of films obtained by evaporating a filament of the metal in high vacuum have been measured. X-ray and microscopic analysis have shown that the metal films thus obtained are crystalline, and that they differ from the bulk metals in having the material in a much more finely divided state. In these three cases the specific resistance is more than 1,000 per cent greater than that of the corresponding bulk metal. The Hall coefficients of the diamagnetic metals are the same as those observed for the metals in bulk. Evaporated iron, however, has a Hall coefficient about 600 per cent greater than the accepted value for pure bulk iron. This leads to the view that the maximum value of the intensity of magnetization is less in evaporated than in bulk iron. The results appear to bear upon recent atomic theories and upon the nature of ferromagnetism.

3. The change in thermoelectric power of tin at the melting point. T. R. HARRISON, Champion Porcelain Company, and PAUL D. FOOTE, Bureau of Standards.—By use of a special potentiometric measuring system of high precision, in which parasitic

e.m.f.'s have been reduced to a minimum so that readings may be made with an accuracy of one tenth microvolt, the thermoelectric power of a solid tin-liquid tin thermocouple at the melting point of tin has been determined and found to be 1.2 microvolts/degree C, the liquid tin being at the higher potential. The computed value of the Peltier e.m.f. is 0.6 millivolt. Both results have a sign opposite to that predicted on the basis of the simple electron theory.

4. Magnetic and natural rotatory dispersion in absorbing media. E. O. HULBURT, University of Iowa.—A *theoretical discussion* based on the electron theory of H. A. Lorentz yielded formulas for the magnetic rotatory dispersion in isotropic absorbing media and for the natural rotatory dispersion in optically active absorbing media. In a few instances where sufficient data enabled calculation, the new magnetic rotation formula has given accurate agreement with experimental values, thereby accounting for the discrepancy previously noted between the observed Verdet angles and those calculated from a theory which neglected absorption.

5. A second undamped wave method of measuring dielectric constants. A. P. CARMAN and G. T. LORANCE, University of Illinois.—The oscillating circuit used in this method consists of an audion with an inductance L and capacity $C_1 + C_2$ in the grid circuit. In the plate circuit with its e.m.f. E_p, there is inserted a galvanometer and in parallel with the galvanometer there is a counter e.m.f. and resistance, forming what has been called by J. J. Dowling (*London Engineering*, Sept., 1921) a "zero shunt." By this arrangement, it is possible to use a sensitive mirror galvanometer to measure small changes in the plate current. Curves were drawn, showing the changes of the mean plate current with changes of the capacity $C_1 + C_2$ for various constant plate voltages and couplings. A part of such a curve shows a linear relation between the mean plate current and the capacity. In the curve used in most of our measurements, there is a linear relation between the mean plate current and the capacity for capacities from 1000 cm to 3500 cm, and a change of 1 cm of capacity corresponds to a change of 2.1×10^{-7} amperes. The galvanometer used has a sensitiveness of 2×10^{-9} amperes per scale division. It is thus possible to read directly with the above arrangement a change of capacity of a hundredth of a centimeter. This sensitiveness can be increased but the arrangement is more sensitive than called for by the present calibration of our reference condensers. This method has been tested by determining the *dielectric constants of a number of gases.* Some preliminary values at 18° C and 76 cm are: for air, 1.000601; for CO_2, 1.000990; for illuminating gas, 1.000772.

6. Comparison of resistance changes in transverse and in longitudinal magnetic fields. W. H. SANDERS and A. P. CARMAN, University of Illinois.—Measurements were made on *copper, silver, manganin, and Advance wire* in both transverse and longitudinal magnetic fields of 4 to 16 kilogausses. The wire was wound about a thin strip of mica so that the field was transverse or parallel to the specimen when the plane of the strip was perpendicular or parallel, respectively, to the lines of force. The field was produced by a DuBois half-ring magnet and the resistance changes were measured by a Wheatstone bridge deflection method. The accuracy of the measurements is estimated to be about 5 per cent for $H = 10{,}000$ gausses with a somewhat greater error probable in the case of weaker fields. The accompanying table shows the ratio of the change in resistance to the resistance in zero field, $\Delta R/R \times 10^5$, all measurements being made at about 23° C. It should be noted that for copper and silver the change is an increase, while for the alloys manganin and Advance the change is similar but of opposite sign.

Metal.		Field Strength in Kilogauss.						
		4	6	8	10	12	14	16
Copper.....	trans.	+0.5	1.0	1.80	2.87	4.00	5.25	6.45
	long.	+0.5	0.96	1.53	2.24	3.20	4.31	5.70
Silver.....	trans.	+0.4	0.84	1.58	2.50	3.56	4.80	6.30
	long.	+0.24	0.52	1.06	1.83	2.62	3.50	4.56
Manganin.....	trans.	−0.17	−0.37	−0.64	−0.92	−1.28	−1.80	−2.30
	long.	−0.12	−0.25	−0.50	−0.80	−1.17	−1.71	−2.22
Advance.....	trans.		−0.48	−0.81	−1.20	−1.75		
	long.		−0.45	−0.80	−1.19	−1.71		

7. The measurement of the dielectric constant and magnetic susceptibility of gases by high frequency methods. E. C. FRITTS, University of Illinois.—A modification of the undamped wave method of Hyslop and Carman (PHYS. REV., **15**, 243, 1920) for determining dielectric constants has been developed by which the beat frequency between two oscillating circuits can be recorded photographically. The frequency of a tuning fork is recorded simultaneously, and this enables any change in the frequency of one circuit, the other remaining constant, to be measured up to 2,000 cycles per sec. By using as a part of the capacity of one circuit a condenser in which the pressure of the gas dielectric is varied from zero to one atmosphere, and recording the resulting change of frequency, the dielectric constants of O_2, H_2, N_2, and CO_2 at a frequency of 800,000 have been found to be 1.000460, 1.000221, 1.000505, and 1.000876, respectively, for one atmosphere at 0° C. These measurements were made for use in correcting the results of experiments of a similar nature for determining the magnetic susceptibility of gases, which are now in progress.

8. A derivation of Planck's law of radiation by means of the adiabatic theorem. JACOB KUNZ, University of Illinois.—The adiabatic theorem, suggested at the first Solvay Congress in 1911, has been worked out in considerable detail by P. Ehrenfest. This theorem, together with a modification in the Maxwell-Boltzmann distribution law and a theorem due to Rayleigh and Jeans, leads to a very short demonstration of Planck's law of radiation.

9. The general law for the distribution of energy in a system of particles. WORTH H. RODEBUSH, University of Illinois.—Lewis and Gibson (PHYS. REV., **15**, 522, 1920) have derived the law for the distribution of kinetic energy in a system of particles of equal masses by a consideration of the cross section of the constant energy surface in a generalized space where Liouville's theorem is applicable. For particles of different masses and for potential energies which are quadratic functions of the coördinates, the constant energy surface will not be spherical but may be made so by a transformation of coördinates. The expression derived by Lewis and Gibson for the probability that any coördinate will have a quantity of energy within specified limits will now be valid if we correct for the change in cross section of the constant energy surface with the transformation of coördinates. Since the modulus of transformation in this case is a constant for any coördinate, the cross sections of the constant energy surface will simply be multiplied by a constant throughout and there will be no change in the relative distribution as expressed by the cross section for any value of a given coördinate. We then obtain the ordinary distribution law which leads to the equipartition value for the average energy of any group of coördinates taken at random. If the potential energy is not a quadratic function of the

coördinates, the case is more complicated but may still be evaluated for simple functions.

10. An optical chronograph. L. THOMPSON, Kalamazoo College.—An optical chronograph, consisting of a falling projectile upon which is mounted a small photographic plate, is released from a holding electromagnet by a pendulum control circuit. A beam of light, focused at suitable points in the trajectory of a body under observation, produces a final image of the slit source in the plane through which the chronographic plate passes. Interruptions of the beam by the body in its flight record the time of the event on the plate, the time being given directly, without the use of auxiliary apparatus for calibration, by the height of fall. In case of extreme precision requirements in the measurement of the longer intervals, for example those of the order of a hundredth of a second involved in certain air resistance experiments for which this chronograph was developed, it is necessary to consider the variation of the force effective in accelerating the chronograph projectile. This is determined experimentally by weighing the chronograph projectile at different positions near the holding magnet, having proper currents in the coil. These are given by an oscillograph record of the current while the circuit is being broken. A simple graphical integration leads to an accurate value for the difference in time between events registered on the chronograph. The effect of air resistance has been calculated on the basis of a linear resistance-velocity relation (very low velocities), the constants being obtained by measurements on the chronograph when placed in a small wind tunnel. Under ordinary circumstances this factor does not introduce a significant error. As the time intervals measured are small compared with the total time of fall, an error in the determination of the total height of fall to the first interruption is of relatively small consequence. The lengths between the interruptions are required with limiting precision, and the records are convenient for accurate comparator work, being on short glass plates which are not subject to the uncertain temperature and development variations of the film surfaces ordinarily used with drum chronographs.

11. The projection of polarized light phenomena. LLOYD W. TAYLOR, University of Chicago.—There seems to be a scarcity of facilities for easy demonstration of the simpler phenomena of polarized light before large groups. A device for filling this need with but little more preparation than is involved in showing lantern slides is presented. The objective of a stereopticon is removed and the emergent light rendered parallel by adjustment of the condensing lens. Two glass-plate piles, preferably somewhat larger than those associated with the usual polariscope, are interposed in the parallel beam at the polarizing angle, one of them being capable of rotation about an axis parallel to the direction of the beam. The specimen to be projected is mounted between them and a simple converging lens of sufficient aperture and appropriate focal length, 20 to 30 cm, is placed in front of the combination to act as the objective. Nearly all the phenomena observable in the conventional type of polariscope may be thus projected. With the aid of a confocal pair of lenses (convex and concave) the arrangement effectively projects the rings and brushes produced by the passage of convergent polarized light through a crystal cut perpendicularly to the optic axis. For convenience the combination should be placed in a properly designed mounting so that it may be handled as a single unit.

12. Sound transmission of sawdust concrete. DANIEL L. RICH and CARL R. BROWN, University of Michigan.—Several slabs of reinforced concrete, all of the same external dimensions but with varying amounts of sawdust ranging up to fifty per cent were cast and permitted to dry thoroughly. It was thought that the sawdust in drying and shrinking would leave a porous slab of concrete of sufficient strength yet much lighter than solid concrete, lighter even than cinder concrete, and that perhaps the porous concrete might transmit sound less readily. To test this, a sound-

proof box was made of two separate wooden boxes, one nesting in the other, with the 15-cm space between the boxes filled with alternate layers of sand and felt. The inside of the inner box was lined with felt, and the edge around the open top of the combination box was covered several inches deep with felt; then a concrete slab to be tested was laid on top of all, the boxes forming a well-insulated cavity of several cubic feet capacity on the under side of the slab. From this cavity an insulated rubber tube was run into an adjacent sound-proof room. One observer was stationed in the sound-proof room while the other produced sounds by dropping a weight through recorded distances on to the top of the slab. Correlation between signals that were audible and heights through which the weight was dropped were found. While the difference in sound conductivity among the various slabs was slight, the observations seemed consistently to indicate that the slabs containing the larger percentages of sawdust instead of being poorer conductors were actually better conductors of sound than the solid concrete.

13. Eliminating interfering sounds in a telephone-transmitter stethoscope. R. B. ABBOTT, Purdue University.—By the use of a telephone transmitter with its diaphragm tuned to some low natural frequency, very faint sounds of low frequency have been detected and amplified to audibility with a vacuum tube amplifier, without interference from higher pitched notes. This type of transmitter is very sensitive to sounds of low frequency and unresponsive to those of higher frequency. A very thin aperiodic diaphragm attached to the opening of the mouthpiece converts this transmitter into a very efficient stethoscope for listening to faint sounds of the human body, because these sounds are of low frequency. In fact, by tuning the diaphragm to frequencies of 100 per second or less, the troublesome interference due to sounds of extraneous sources, heretofore experienced, is almost entirely eliminated and the sound of heart beats becomes very clear and distinct. By combining such an apparatus with a three-step vacuum tube amplifier and a loud speaking telephone, the sound of heart beats has been made audible so that hundreds of persons assembled in a large audience room heard it clearly and with ease, phonograph records of heart beats have been made which reproduce the beats with perfect accuracy and clearness, and heart beats have been broadcasted by radiophone and heard with perfect ease by hundreds of persons listening in at receiving stations.

14. The cause of the optimum angle in a receiving conical horn. VICTOR A. HOERSCH, University of Iowa.—Observers have found the amplification of pressure at the vertex of conical horns at resonance to incident waves of constant frequency to have a maximum at a certain angle, termed the optimum angle. A theoretical explanation is possible upon the assumptions (1) that the apparatus for measuring the amplification at the vertex absorbs energy from the horn, and (2) that the vibrations within the horn are of spherical wave type with node at the origin and the open end approximately a loop. If we equate the energy put into the horn by both the incident wave and the wave reflected from the plane of the open end to the energy radiated from the opening of the horn plus the energy absorbed by the apparatus attached to the vertex, we get an expression for the velocity at the opening of the horn which, when substituted in the expression for the amplification of pressure, gives the result that the amplification is a maximum when the angle is such that the radiation from the open end equals the absorption of energy at the vertex. The agreement with experiment seems good.

15. The action of horns as sound amplifiers. ARTHUR L. FOLEY, University of Indiana.—Complete paper appeared in the PHYSICAL REVIEW, 20, 505–512, December, 1922.

16. The dynamic theory of an acoustic diaphragm and its application to sound analysis. MAX MASON, D. L. HAY, and L. B. SLICHTER, University of Wisconsin.—

The motion in air of a rigid diaphragm which drives a mechanism, such as a rotating mirror, without lost motion or internal vibrations, is considered. The two sides of the diaphragm form partial boundaries for air cavities of volumes v_1 and v_2, from which long tubes of cross section s_1 and s_2 lead away. Under these circumstances the displacement of the diaphragm may be theoretically studied as the solution of a differential equation of the fourth order. The theoretical behavior is discussed, as determined by the parameters, v_1, v_2, s_1, s_2, and the mechanical parameters of the system. The theory is compared with the results of observations on an instrument which was built to satisfy the assumptions made. A diaphragm of sufficient stiffness was formed by a spun aluminum cone. The cone carred at its vertex a small phosphor bronze rod which rested upon the upper edge of a steel shaft of square cross section, the shaft being rocked by the motion of the rod. The lower edge of the shaft rested on a copper block. The shaft carried a small mirror by means of which the motion was photographically recorded. This system was free from lost motion and contained no internal free vibrations of frequency below 20,000 per second. Comparison with the theoretical results was made for special values of the volumes and outlet cross sections, by studying the free motion of the diaphragm after impulse excitation, produced by the sound of a spark. The curves showed in the main a satisfactory agreement with the theory and indicate that acoustic parameters may be accurately calculated from the theory and that the instrument may be used as a dependable means of absolute measurements.

17. Reverberation in auditoriums. F. R. WATSON, University of Illinois.—Sabine's formula for reverberation gives the time of decay of a standard sound in an auditorium in terms of the volume and absorbing power. To correct a defective auditorium or to design the acoustics of a new one, it is necessary to know the actual time of decay that will give the best effect. The author has made a study of a number of auditoriums and has found a relation indicating that the time of decay varies approximately with the cube root of the volume. A further relation follows from this showing that for best effect the energy of the sound generator should vary with the square of the cube root of the volume. Curves are drawn showing data for actual auditoriums.

18. Acoustic wave filters; attenuation and phase factors. G. W. STEWART, University of Iowa.—If a filter consists of a conduction tube with equally spaced branches containing like inertances and capacitances, the value of the attenuation factor, α, in the region of attenuation is obtained by the formula, $\cosh \alpha = \pm (1 + Z_1/2Z_2)$, Z_1 and Z_2 being the impedances in each section in the tube and in each branch, respectively. The proper sign will give a positive value for $\cosh \alpha$. In this same region, the decrease in phase, ϕ, at each branch point will be either zero or π. If zero, the sign in the value of $\cosh \alpha$ is positive and if π, it is negative. ϕ may change discontinuously from zero to π or vice versa, but only when the attenuation factor is infinite and the transmission zero. The variation in α in the frequency regions of attenuation is discussed and it is found that α never becomes zero. The value becomes infinite when the frequency is the natural frequency of the side branch. A special case of this is the well-known resonating branch tube which is incorrectly said to "absorb" the sound. The value of ϕ within the frequency region of no attenuation, $\alpha = 0$, always varies continuously from zero to π. The discussion shows that the preferences given in a previous article (PHYS. REV., 20, 528, December, 1922) to certain approximate formulæ for the frequency limits of no attenuation are confirmed.

19. Predicted transmission curves of acoustic wave filters. H. B. PEACOCK, University of Iowa.—A test was made of the theory of G. W. Stewart concerning the variation of α, the attenuation factor, in the transmission of certain acoustic wave filters. This was accomplished by predicting the transmission curves and comparing

with the experimental values. Three filters were used, a low-frequency pass, a high-frequency pass, and a single-band pass. The constructed transmission curves agree with the experimental values in a fairly satisfactory manner, considering the necessarily approximate character of the theory. (Compare preceding abstract, 18.)

20. The spectrum of helium in the extreme ultra-violet. (THEODORE LYMAN, Harvard University.—In continuation of previous work, a vacuum spectroscope has been built which enables a good vacuum to be maintained in the body of the apparatus while the pressure of the helium in the discharge tube is as great as a millimeter. No window was employed, the success of the device depending on the use of a very short and narrow slit and upon the application of a powerful pump. With a continuous current the line at 584.4 A is of very great strength and is accompanied by three new lines at 537.1, 522.3, and 515.7 whose intensities decrease with their wave-length and in a manner strongly suggesting a series relation. Comparison with hydrogen lines has given the wave-lengths probably within one or two tenths of a unit. The spacing on the frequency scale is such that these lines are clearly the first four members of a new principal series which, according to the notation of Fowler, is to be designated by $oS - mP$. The limit of this series can be accurately calculated and is found to correspond to 24.5 volts, whereas the experimental value of the ionization potential of helium is 25.3 volts. Comparison with the resonance potentials determined by Franck and Knipping shows that if a correction of about — 0.8 volt is applied to their measurements, the potentials are brought into fair agreement with the individual wave-lengths but at the expense of the first resonance potential which is left without any corresponding line in the spectrum. There is also a single line at 600.5 $\pm$ 0.3 of a feeble and diffuse character, but its origin is not entirely above suspicion.

21. Intensity relations in the hydrogen spectrum produced by electron impacts. A. LL. HUGHES and P. LOWE, Queen's University.—In almost all experiments hitherto made, the intensities in the spectrum have been studied as a function of such variables as the pressure, the purity of the gas, the presence or absence of a condenser, etc. The fundamentally important factor in the excitation of an emission spectrum, however, is the collision between an electron and a molecule, for this is the process whereby an atom or molecule is put into a state in which it can radiate. Hence, the distribution of intensity in the hydrogen spectrum produced by the impact of electrons was studied quantitatively for electron energies between 29 and 110 volts. A three-electrode tube was used, the electrons being acclerated quickly from the oxide-coated filament to a grid close by and then into a field-free space between the grid and a plate. The spectrum of the light from this space was photographed for different accelerating voltages, and the densities of the first four series lines and of twelve prominent secondary lines were measured by a microphotometer. *Four series lines.* The density of Hα remains practically constant over the whole range, while the densities of Hβ, Hγ, and Hδ increase at first rapidly and then tend to a constant value as the energy of the electron is increased from 29 to 110 volts. The density change is greater the higher the term number. *Twelve secondary lines.* The densities of the band lines $\lambda\lambda$ 6327, 6225, 6135, 6122, 6030, and 6018 decrease exceedingly rapidly as the energy of the electron is increased from 29 to 110 volts, while the densities of $\lambda\lambda$ 5013, 4934, 4929, 4632, 4743, and 4205 show a definite maximum between 30 and 40 volts, and then decrease rapidly, but not so rapidly as the first six lines. From the relative behavior of the series spectrum and the secondary spectrum it is inferred that the *proportion of dissociating collisions to non-dissociating collisions* increases rapidly with the energy of the impacting electrons between 29 and 110 volts, and, from the intensities of the series lines, that the higher the energy of impact the more likely is the electron within the atom to be displaced to the remoter Bohr orbits as the molecule is being dissociated by electron impacts.

22. On the vacuum spark spectrum of silicon, λ 2100–λ 6700. R. A. SAWYER and R. F. PATON, University of Michigan.—A preliminary investigation on the vacuum spark spectrum of silicon (PHYS. REV., 19, 256, 1922) showed many new lines in the spectrum of silicon in the region λ 6700–λ 4070. In a continuation of this work a liquid air trap has been used to freeze out the vapors from the mercury pumps and better vacua with correspondingly more intense sparks have been obtained. The previous results have been verified and extended, using the 60° flint glass prism spectrograph of the Littrow type which was previously described. Data have been obtained also in the region λ 4070–λ 2100 by use of a quartz spectrograph designed and built in the course of this work. It is of a type first described by Fabry and Buisson (*J. de Phys.*, 9, 929, 1910), with the slit directly over the prism. The entering radiation is collimated by a platinized concave mirror of 33-inch focal length and after traversing the 60° quartz prism is brought to a focus on a photographic plate by a single quartz lens. The region λ 6500–λ 2100 was photographed on a 10-inch plate inclined at 45° to the axis of the camera. An iron arc was used as a comparison source and it is believed that the accuracy is at least 0.1 A in the regions λ 5500–λ 4070 and λ 3200–λ 2100; and at least 0.2 A in the regions λ 6700–λ 5500 and λ 4070–λ 3200. Over 700 lines were measured. Nearly 400 of these have been identified as due to impurities, chiefly iron, calcium, and aluminum. The remaining lines are attributed to silicon. They include most of the 80 lines previously attributed to silicon and over 200 new lines of which about 100 are very faint and so are classified as doubtful. The vacuum spark appears to be the most powerful source yet used for producing the spectrum of highly resistant or easily oxidizable metals.

23. Relative intensities of helium lines as a function of current. BESSIE CURRY, University of Chicago.—The change in intensity of the lines within a series in the spectrum of helium, as related to changes in exciting current, was investigated by means of a Brace-Lemon spectrophotometer. The results obtained confirm Kayser's early observation of a shift of energy toward the violet, but they do not show even qualitative relations to the Wien displacement law of black body radiation, as suggested by him. The current intensity curves are all of the form $y = ax^n$, where a and n are constant for a given line between definite limits of the current, changing abruptly at certain critical values.

24 Luminescence of organo-magnesium halides. R. T. DUFFORD, S. CALVERT, and DOROTHY NIGHTINGALE, University of Missouri.—Luminescence among compounds of the type RMgX (Grignard Reagents) has been studied to determine the factors affecting the intensity and wave-length of the radiation. Of a large number of compounds studied, about thirty have so far been found to exhibit *chemi-luminescence on oxidation* with O_2. Less than ten of these have been mentioned in the literature previously. Experiments with this oxidation reaction led to the following conclusions: (1) The concentration of the solution affects the intensity, the best results occurring with fairly strong solutions. (2) While these compounds are almost invariably prepared in ethyl ether, this ether is not at all necessary. The compounds can be prepared, and are at least as luminescent, in several other solvents, which contain no trace of ether. (3) Slight changes of temperature have little effect on the light. (4) The magnesium in the compound is necessary; the analogous zinc compounds show no light when oxidized. (5) Most aliphatic compounds (not all) are not luminescent, while many aromatic compounds (not all) are active. (6) Changing the reacting halogen affects both color and intensity of the emission; the lighter the atomic weight, the longer the wave-length, and in some cases also the greater the intensity. (7) In aromatic compounds, a second substituent in the benzene ring affects markedly both color and intensity of the radiation. The position of the substituent in the ring usually has a small effect, which in certain cases is large, para

compounds being generally brighter than ortho or meta compounds. The nature of the substituent has a large effect. Some series of groups show an increase of intensity with increasing formula-weight, while in most cases the reverse is true. The color usually shifts to longer wave-lengths with decreasing weight in any one series, such as the halogens. (8) Mass or molecular weight is not the determining factor for either effect. (9) The oxidation of p-ClC_6H_4MgBr is remarkably bright, probably the brightest case of chemi-luminescence on record. (10) Unsaturation of the molecule is not alone sufficient to produce the luminescence. (11) Certain unsaturated aliphatic compounds are luminescent. (12) The condition that the MgX group be attached to an unsaturated carbon atom seems to be necessary, and at least in most cases is sufficient, to produce the luminescence. Other compounds are being studied to verify this suggestion.

Many such compounds are found to show chemi-luminescence when reacting with chlorpicrin and with brompicrin, as in the well-known Wedekind reaction. The radiation from this reaction is not identical with that obtained by direct oxidation, but is generally of longer wave-length. It is of interest to note that a large number of these compounds and their oxidation-products are found to be fluorescent in ultraviolet light.

25. The low voltage mercury arc. M. SCOTT, Cornell University.—It is fairly well established that in arcs of this type the striking potential decreases with increasing filament current, and recently K. T. Compton (PHYS. REV., **20**, 283, 1922) has shown that the striking potential plus initial velocity in volts decreases with increasing filament current. In recent experiments the author has corroborated the decrease in striking potential with increasing filament current, and in addition has studied the *variation in striking potential with temperature* of the experimental tube. It was found that if the filament current be maintained constant and the vapor pressure of the mercury be varied by changing the temperature of the tube, the striking potential decreases with rise in temperature in much the same fashion as with increasing filament current. For example, if the filament current is not too high, the striking potential may decrease six or seven volts as the temperature of the tube increases from 120° to 250°, corresponding to a change in vapor pressure from 1 mm to 75 mm.

26. Electronic bombardment of metals. H. E. FARNSWORTH, University of Wisconsin.—The method of electronic bombardment of nickel, as explained in a recent paper (PHYS. REV., **20**, 358, 1922) has been extended to *copper and gold*. The former apparatus was used and targets of the above metals were inserted. The curves obtained by plotting the ratio of the secondary to the primary current as a function of the accelerating primary voltage for nickel, copper, and gold, subsequent to baking at 400° C for several hours but previous to heating at bright red heat, are somewhat similar in form, the copper and nickel curves being more nearly identical. As in the case of nickel, the results for copper and gold were materially changed by heating the targets to bright red heat, but the limiting curve obtained is quite different for each metal. (1) For copper, the curve has three distinct maxima at about 2.5, 6.5, and 13.0 volts primary velocity, but outside the region of these maxima, was not changed appreciably. Measurements of the velocity distribution of the secondary electrons from copper indicate that when the primary velocity is as great as 100 volts the bulk of secondary electrons have velocities corresponding to a few volts, but there are a few per cent with velocities nearly equal to that of the primary electrons. For the lower primary velocities the bulk of secondary electrons seem to have velocities more nearly equal to that of the primary electrons, although no difference could be noticed in the distribution for primary velocities corresponding to the position of the various maxima. (2) Because of the ease with which gold evaporates at red heat temperature, the gold target could not be given as much heat

treatment as the other targets. The general shape of the curve for gold before and after red heat treatment is much the same, but the effect of the heat treatment is to considerably reduce the secondary electron current. The curve is of much the same form as that for nickel and copper before red heat treatment, except for a pronounced dip between 3.5 and 11.5 volts primary velocity.

27. The probability of inelastic collisions of electrons in mercury vapor. JOHN A. ELDRIDGE, University of Wisconsin.—It is known that while the majority of collisions of electrons in mercury vapor are elastic, collisions do occur with energy losses of 4.9 volts and 6.7 volts corresponding to the spectrum lines λ 2536 and λ 1849, but little of a quantitative nature is known about the relative number of these collisions. By means of the type of tube previously described, it is possible to measure the relative number of electrons which, having entered the vapor region with any desired velocity and made a large number of collisions, have in that region suffered no inelastic collision, or have made one or more collisions involving an energy loss of 4.9 or 6.7 volts. Thus, curves have been obtained, giving the probability of the two types of inelastic collision as functions of the incident velocity. The number of 4.9-volt collisions shows a very strong maximum when the energy of impact just exceeds 4.9 volts and at the higher voltages is almost negligible. This behavior corresponds to a true resonance phenomenon and is in marked contrast to the results for the 6.7-volt collisions. For these, the probability is very small until the energy of impact reaches about 14 volts, then rises to a maximum (about 25 volts) and appears to decrease slightly as the voltage is still further increased. Assuming the truth of the Bohr conception of these phenomena, the present experiments give what Seeliger calls the excitation functions of the resonance spectra of mercury.

28. Atomic radii. MAURICE L. HUGGINS, Harvard University.—Defining the atomic radius as the distance from nucleus to valence electron-pair, considering only crystals in which these electron-pairs are on the centerlines between adjacent atoms, and transferring radii from one crystal to another only when the arrangements of valence electrons and of atomic kernels around the atom in question are very similar in the two cases, *atomic radii of nineteen elements* have been computed by W. L. Bragg's method, in which the distance between two adjacent atomic centers is taken to be equal to the sum of the two atomic radii. The following radii in Ångstroms have been obtained: Be, 1.00; C, 0.77; O, 0.65; Mg, 1.29; Si, 1.17; S, 1.04; Cl, 0.96; Mn (divalent), 1.39; Fe (divalent), 1.23; Cu (monovalent), 1.42; Zn, 1.31; Ge, 1.22; Se, 1.12; Br, 1.10; Ag, 1.60; Cd, 1.49; Sn, 1.40; Te, 1.23; I, 1.22. To make them strictly comparable, the radii given are for crystals in which each kernel of the given atom, with a net charge $+n$, is surrounded by four valence electron-pairs bonding it to four kernels of other atoms, each having a net charge $(8-n)$. The radii of C, Si, Ge, and Sn are taken as half the interatomic distances in crystals of the elements. The S radius (when surrounded by four positive divalent elements) is assumed to be 1.04 A, 0.01 A less than half of Ewald's determination of the S-S distance in pyrite. If this is lower than the true value, then all the radii given above for electronegative atoms are the same amount too low and those given for electropositive atoms are too high; and vice versa. The O, Se, and Te radii are obtained by comparing the interatomic distances in ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, and HgTe, assuming the radius of the metal atom to be constant in each series. The Zn, Cd, and Hg radii are obtained from the same series of compounds. The Be radius is calculated from the Be-O distance in BeO. Taking the Zn-O distance in $ZnCr_2O_4$ to be the same as in ZnO, the Cr-O distance in that compound is computed; and transferring that to $MgCr_2O_4$, the Mg-O distance is obtained, and so the Mg radius. Similarly the radii of divalent Mn and Fe atoms are calculated from the dimensions of the spinels, and

a check on the Cd radius is obtained. The I radius is assumed to be 0.01 A less than that of Te. The Ag and Cu radii are obtained from their iodides and then the Cl and Br radii from CuCl and CuBr. Although there are no crystallographic data available on the halides of monovalent gold, the density of AuCl has been determined. Assuming this substance to possess a structure either like the hexagonal form of AgI or the cubic forms of AgI and the copper halides, the Au-Cl distance is calculated, and from this the Au radius. This comes out to be practically the same as the Ag radius, just as the Hg radius is found to be practically equal to that of Cd, an agreement which would hardly occur if the assumed structure were incorrect. The *radius of the hydrogen atom* in ice, where each hydrogen is bonded by electron-pairs to two oxygen atoms, is 0.73 A. In the centered-cubic forms of NH_4Cl and NH_4Br the hydrogen diameter is computed to be 1.67 A (NH_4Cl) and 1.64 A (NH_4Br).

29. On the principal optical constants of isolated tellurium crystals. L. P. SIEG and G. D. VAN DYKE, University of Iowa.—By utilization of the "Crystelliptometer" (Weld, *J. O. S. A. and R. S. I.*, **6**, 67, 1922), the principal optical constants for isolated tellurium crystals have been determined for several wave-lengths in the visible spectrum. These constants are: R_1 and R_2, the principal reflecting powers; n_1 and n_2, the principal indices of refraction; and k_1 and k_2, the principal absorption constants. The subscripts 1 and 2 indicate the values of the constants obtained when the light falling on one of the hexagonal faces is polarized with the electric vector respectively parallel and perpendicular to the principal crystalline axis. The tellurium crystals studied are long, slender, lustrous hexagonal prisms, very similar in appearance to the selenium crystals used by Weld. The principal constants are clearly distinct from one another, but are not so different as the corresponding constants for selenium crystals. The ranges in the visible spectrum are: for R_1, 0.28 to 0.34; for R_2, 0.26 to 0.30; for n_1, 2.50 to 3.44; for n_2, 2.05 to 2.68; for k_1, 0.40 to 0.56; and for k_2, 0.54 to 0.67. (Compare Van Dyke, *J. O. S. A. and R. S. I.*, **6**, 917, 1922.)

30. The crystal structure of quartz. L. W. MCKEEHAN, American Telephone and Telegraph Company and Western Electric Company.—The space-lattice of quartz, proposed by previous experimenters, is confirmed by the powder method of x-ray crystallometry. The positions of the atoms are determined with a fair degree of accuracy by the relative intensities of the lines in the pattern. The molecule of silica is easily distinguished, the distance between atom-centers in a molecule being less than that between atom-centers in adjacent molecules. The space-group is D_3^3 or D_3^5, the space-lattice being Γ_h, with $a = 4.89 \times 10^{-8}$ cm, $c = 5.375 \times 10^{-8}$ cm. The distance between adjacent unlike atom-centers in the molecule SiO_2 is 1.63×10^{-8} cm, that between adjacent unlike atom-centers in different molecules is 2.18×10^{-8} cm. The molecule forms an obtuse-angled isosceles triangle, the obtuse angle at the Si atom-center being about 115° 14′. The physical properties of the material are consistent with this unsymmetrical shape of molecule.

31. The scattering of x-rays from crystals at small angles. G. E. M. JAUNCEY and H. L. MAY, Washington University.—Continuing the experiments on the scattering of x-rays by crystals previously described by one of the authors (PHYS. REV., **19**, 435, and **20**, 82, 1922), work has been done on the *scattering at angles between 30° and 4°*. Instead of allowing the primary rays to fall on the crystal face at a glancing angle, the rays were passed through a thin slab of rocksalt, the (1, 0, 0) face of the crystal being placed perpendicular to the primary rays. The thickness of the crystal which under these conditions will give the most intense scattering in the direction ϕ, where ϕ is small, is equal to the reciprocal of the linear absorption coefficient of the primary rays. Using a Coolidge tube with a Mo target operated at 70 KV, the scattering of heterogeneous x-rays between the angles of 2° and 30° was examined.

The intensity increases from 1.0 at 30° to 1.5 at 6°. Passing to the small angle side of 6° there is a sudden drop in the scattered intensity so that at 4° the intensity is only 0.65. Below 4° extraneous scattering from the slits appeared so this range is left for further experiment.

32. A quantum theory of the scattering of x-rays by light elements. ARTHUR H. COMPTON, Washington University.—The hypothesis is suggested that when an x-ray quantum is scattered it spends all of its energy and momentum upon some particular electron. This electron in turn scatters the ray in some definite direction. The change in momentum of the x-ray quantum due to the change in its direction of propagation results in a recoil of the scattering electron. The energy in the scattered quantum is thus less than the energy in the primary quantum by the kinetic energy of recoil of the scattering electron. The corresponding increase in the wave-length of the scattered beam is $\lambda_\theta = \lambda_0(1 + 2\alpha \sin^2 \frac{1}{2}\theta)$, where $\alpha = h/mc\lambda_0$. It is found, also, that the total energy removed from the primary beam by the scattering process is less than that given by J. J. Thomson's classical theory, in the ratio $1/(1 + 2\alpha)$. Of this energy a fraction $(1 + \alpha)/(1 + 2\alpha)$ reappears as scattered radiation, while the remainder is truly absorbed by the recoil of the scattering electrons. The theory indicates also a concentration of the scattered energy in the forward direction. These deductions are shown to be in good accord with the results of experiments on the scattering of x-rays by light elements.

33. Time of imprisonment of resonance radiation in a gas. K. T. COMPTON, Princeton University.—The passage of resonance radiation through a gas may be treated by equations similar to those used in describing the diffusion of foreign gas molecules through the gas, even though the actual amount of physical similarity between the two processes is uncertain. The particular case treated is that of radiation produced (as by electron impacts) in a cylindrical shell between two coaxial cylindrical electrodes. It is found that the total number of excited atoms (atoms which have absorbed but not yet reëmitted a quantum of resonance radiation) is $N = K\alpha^2\tau n$, where n is the number of quanta produced per second by electronic impacts, τ is the average time during which an atom remains excited as the result of absorption of radiation, α is the scattering coefficient of the radiation in the gas and K is a numerical factor which depends on the geometry of the parts. If the electron impacts are suddenly stopped, the time required for the number of excited atoms to fall to any fraction of its initial value depends on $\alpha^2\tau$ and may be calculated. Substitution of probable values for α and τ leads to results consistent with the view that Kannenstine's time, 0.0024 sec., for the persistence of excited atoms in helium (*Astrophys. Jour.*, **55**, 345, 1922) may be accounted for along the lines suggested above, with a value of τ of the same order of magnitude as that measured for other substances, his result thus depending on $\alpha^2\tau$ rather than on τ alone. Other applications are suggested.

34. The electron emission from tungsten, thorium, molybdenum, and tantalum. S. DUSHMAN, H. N. ROWE, and C. A. KIDNER, General Electric Company.—Precision emission data were taken in high vacuum on carefully pyrometered filaments. Corrections were introduced for lead losses and for the Schottky effect, that is, the increased emission due to the potential gradient at the cathode. Results obtained are in very satisfactory agreement with the equation: $I = 60.2T^2\epsilon^{-b_0/T}$ amps/cm² which was deduced by one of the writers in a previous communication (PHYS. REV., **20**, 109, 1922). The temperature scale used was that of Worthing and Forsythe. The values of b_0 and the emission in amps/cm² at $T = 2{,}000K$ are as follows:

	b_0.	$I(T = 2{,}000)$.	ϕ_0.
Tungsten	52,600	9.12×10^{-4}	4.53
Thoriated tungsten	34,100	9.55	2.94
Molybdenum	50,000	3.31×10^{-3}	4.31
Tantalum	46,500	1.95×10^{-2}	4.01

The equivalent values of ϕ_0, the *work-function*, are given in the last column. Data recently published by Davisson and Germer (PHYS. REV., **20**, 300, 1922) on the electron emission for tungsten are found to be in excellent agreement with the above equation, and the corrected value of b_0 obtained by them is 52,300, which agrees within the limits of experimental error with the value given in the table.

35. Characteristics of a short wave oscillator. L. L. NETTLETON, University of Wisconsin.—A rather extensive study has been made of the characteristics of a vacuum tube when oscillating at very high frequencies. The oscillation is of the type discovered by Barkhausen and Kurz, the frequency of which seems to depend only on the dimensions of the parts of the tube, and on the voltages applied. The tube used has a symmetrical cylindrical arrangement of filament, grid, and plate, and was left permanently connected to the vacuum pumps so that observations could be made at very low pressures. The wave-lengths were from 50 to 200 centimeters. The outstanding feature of a tube when oscillating in this manner is that there is a negative current to the plate, which may be as much as one fourth of the total electron current from the filament to the grid; or if the plate current is left open and its potential measured with an electroscope, there is a negative potential which may rise to as much as 150 volts, with a positive potential of from 300 to 500 volts on the grid. This negative plate current may be present apparently with little or no oscillation in the Lecher wires by which the wave-lengths were measured. The characteristics of the negative plate current and potential, and of the accompanying oscillations have been studied as a function of grid voltage, of electron current, and of gas pressure. The phenomenon apparently is not purely electronic, but requires a small amount of ionization for its manifestation, since at very low pressures all signs of oscillation and of plate current and potential cease very suddenly, the critical pressure being lower for higher electron currents. For air, the critical pressure, as measured with an ionization manometer, varied from .00001 to .00005 mm.

36. The thermionic work function of oxide-coated platinum. C. DAVISSON and L. H. GERMER, American Telephone and Telegraph Company and Western Electric Company.—The authors have described measurements (PHYS. REV., **20**, 300, 1922) upon a single tungsten filament which yielded accurate values of ϕ, the equivalent voltage of the thermionic work function determined calorimetrically, and b, the exponent in Richardson's equation. Similar measurements have now been made upon a filament of pure platinum coated with the oxides of barium and strontium. ϕ and b for this filament at 1064° K satisfy the theoretical relation $\phi = bk/e$ within less than one per cent, which is less than the possible error of each measurement. It was found that when the filament temperature was suddenly changed the emission did not become steady immediately, but changed gradually from an initial to a final value. The agreement mentioned above is for b reckoned from initial values of emission for sudden changes from the "standard temperature" 1064° K. A measurement of bk/e for "standard temperature" 911° K gave 1.59 volts, a value 11 per cent less than that found for 1064° K (1.79 volts). This decrease in work function was accompanied by a decrease in the A constant of Richardson's equation to one fifth its value at the higher temperature. Final as well as initial values of emission were found to satisfy Richardson's equation.

37. Positive ray analysis of potassium and calcium. A. J. DEMPSTER, University of Chicago.—With the apparatus described in former papers, isotopes of potassium were measured at atomic weights 39 and 41, thus confirming the results obtained by Aston. Two different sources were used, water glass and a mixture of lithium and potassium. The ratio of the intensities was about 18 to 1. In a previous paper the calcium line at 40 was found to be accompanied by a faint component at 44. To decide whether this was due to calcium or carbon dioxide, a sample of calcium was prepared by distillation in vacuo, and this also gave the 44 line, thus proving that it is an isotope of calcium. The intensities gave a mean mass agreeing with the chemical atomic weights.

38. Alkali vapor detector tubes. CHAS. T. KNIPP and HUGH A. BROWN, University of Illinois.—Previous work by the authors (PHYS. REV. **19**, 278, 1922) has shown that three-element vacuum tubes containing gases having low ionizing potentials function efficiently as detectors in radio receiving circuits with very low plate voltages. Continuing the investigation, potassium-sodium alloy, having an ionizing potential of four volts, was introduced by distillation into standard three-element tubes until the inner walls of the bulb acquired a silvery coating of the condensed alloy vapor. Tubes treated in the above manner proved to be from 3 to 5 times as sensitive as the conventional gas content detectors, and also to be even less critical in the adjustments for optimum plate voltage and filament current to give loudest response, than many of the high vacuum tubes. Furthermore, the plate voltage required for best signal response is only 6 to 10 volts. Indeed these tubes are quite sensitive detectors at zero plate voltage, when the plate circuit return is connected to the negative leg of the filament. The characteristic curves of these alkali vapor tubes are very similar to those of high vacuum amplifier tubes, being smooth and straight in regions of negative grid potentials. Plate currents of from .75 to 1.0 milliampere are obtained with zero plate voltage, when connected up as indicated above so as to make the plate negative to a portion of the filament. This plate current, however, flows from the plate to the filament across the intervening space, just as if a positive potential were externally applied to the plate. The source of energy for this plate current has not as yet been satisfactorily explained. It is probably due to the low ionizing potential effects of the alkali vapor, or more remotely to photo-electric effects, or possibly both. These points are under investigation.

39. The luminous electrical discharge in sodium vapor. G. M. J. MACKAY and E. E. CHARLTON, General Electric Company.—Typical results obtained in a spherical bulb of pyrex glass 18 cm in diameter containing a tungsten filament .038 cm in diameter and a nickel disc anode 2.54 cm in diameter, 8 cm apart, with sodium vapor heated to 267° C, and filament at 2500° K giving 54.5 c.p., are given below.

Discharge: volts.....	10	14	19	30	100	200
amperes.....	.081	.223	.525	.810	.475	.510
Candle power of glow....	5.1	27.2	115	201.5	163.5	269.5
Watts/c. p. of glow.....	0.16	0.12	0.09	0.12	0.29	0.38

The presence of the sodium vapor enables enough ionization to occur to remove space charge so that approximately the full electron emission is obtained from the cathode, but the pressure is too low to allow the formation of an arc. It has been found possible on this account to operate a glow discharge in parallel with an ordinary incandescent lamp filament in the same bulb with no short circuiting of the current through the glow. The decrease of luminosity at the higher voltages probably indicates the influence of the applied field in lessening recombination.

The glow which appears under the above conditions uniformly fills the whole bulb. In one experiment the primary bulb was surrounded by a vacuum jacket of glass into

which sodium was introduced but no electrodes. Upon the operation of the inner bulb with the production of a glow, the annular space also showed an equally intense glow demonstrating that the uniform distribution is due to optical resonance of the vapor surrounding the main discharge.

A specific consumption of .09 watts per candle has been obtained for the glow alone. Assuming that most of the light comes from the D lines, the efficiency is shown to be about one third of the ideal.

40. The mechanism of cathode sputtering. K. H. KINGDON, General Electric Company.—In a previous note (Kingdon and Langmuir, PHYS. REV., **20**, 108, 1922) a method was described for studying the removal of thorium from the surface of a thoriated tungsten filament by positive ion bombardment. This method has been applied to *hydrogen, neon, argon, cæsium, mercury, and helium.* Hydrogen shows no sputtering up to 600 volts energy of the ions, but neon, mercury, cæsium, and argon all sputter thorium in the same way. The numbers of thorium atoms sputtered per impacting ion are, respectively, 0.043, 0.092, 0.155, 0.16 at $V = 150$ volts. For these gases the rate of sputtering falls to zero at $V_0 = 45$, 55, 52, and 47 volts, respectively.

From the values of V_0, and the shape of the initial part of the curve connecting time of bombardment with amount of thorium sputtered, the following *theory* of the mechanism of sputtering in these gases has been deduced. The process seems to occur in two steps. First, the impacts of the ions form a large number of depressions in the surface of the cathode without removing thorium; then, ions striking the bottoms of these depressions are reflected and knock off thorium atoms from around the edges of the depressions. In the case of helium, the number of thorium atoms removed per ion is much smaller than for the other gases, and is proportional to V^2 up to 600 volts. The mechanism discussed above does not hold here. Following J. J. Thomson it is suggested that in this case the sputtering is due to the absorption of radiation produced when the He ions are stopped.

41. The luminous efficiency of gases excited by electric discharge. ARTHUR H. COMPTON, Washington University, and C. C. VAN VOORHIS, Westinghouse Lamp Company.—A systematic investigation has been made of the light emitted by *twenty-four elementary gases* per unit energy consumed, when excited by an electric discharge at low pressure. The light was measured from a limited portion of the vacuum tube, and the corresponding electrical energy was determined by measuring the potential drop and the current in this part of the tube. The efficiencies vary from 0 in the case of arsenic vapor to 17 candles per watt in the case of sodium vapor. The maximum observed efficiencies of neon, mercury, and sodium are 1.8, 10, and 17 mean spherical candles per watt, respectively. These three are the only elements which give as high luminous efficiency as do present-day commercial illuminants. It is shown that it is very improbable that any gas composed of polyatomic molecules will have high efficiencies. A consideration of the spectral characteristics shows why the luminous efficiency of mercury vapor increases with the current density, while that of sodium vapor decreases when the current rises above a certain optimum value.

42. Photo-electric cells with hot filaments. J. TYKOCINSKI-TYKOCINER and JACOB KUNZ, University of Illinois.—Experiments were performed with alkali photo-electric cells in which heated tungsten filaments had been introduced, to determine the effect of illuminating the photosensitive layer upon the current flowing between the filament and a gauze acting as an anode. These cells are found to have a greater sensitivity and a lower resistance than similar cells without hot filaments. With the filament cold, the tube acts as an ordinary photo-electric cell, light exciting a current from the filament (anode) to the sensitive alkali layer (cathode). If, however, the filament is gradually heated, the photo-electric sensitivity rises until a definite temperature is

reached for which the sensitivity attains a maximum value. With further increase of the filament temperature the sensitivity decreases until a point is reached when light has no influence whatever. Above this point the influence of light is to increase the plate current so that the sensitivity increases with the temperature once more. The following explanation of the phenomenon is suggested. When cold, the filament is covered with a thin layer of alkali atoms. When the filament is slightly heated these atoms send out positive ions which neutralize the space charge in the tube, thus increasing the photo-electric current. With further increase of the temperature the space in the tube becomes filled with atoms of alkali vapor which bombard the tungsten filament. The collisions at the surface of the filament facilitate the expulsion of thermions and also of photo-electrons when light is acting. This explains why large plate currents are obtained without the application of external potentials.

43. The volt-ampere characteristics of electron tubes with thoriated tungsten filaments containing low pressure inert gas. ALBERT W. HULL and W. F. WINTER, General Electric Company.—A typical tube consists of a 30 mil filament of tungsten with half a per cent of thorium oxide, in the axis of a cylindrical anode 1 inch in diameter and 1 foot long, containing pure argon at 40 bars (.030 mm Hg) pressure. With the filament at 2100° K, the current between cathode and anode increases linearly with voltage up to a maximum of 20 amperes at 25 volts, then decreases rapidly with further increase of voltage, and is essentially zero for all voltages from 100 up to 10,000. This "negative resistance" characteristic is due to the removal of the active layer of thorium from the surface of the filament by positive ion bombardment. Ions of less than 25 volts velocity have no effect, but above 25 volts their ability to knock off thorium atoms increases rapidly with increasing velocity.

44. A direct determination of the principal reflecting powers of isolated tellurium crystals. L. P. SIEG, University of Iowa.—The apparatus employed in determining the principal reflecting powers of individual selenium crystals (*J. O. S. A. and R. S. I.*, **6**, 448, 1922) has been used in making measurements on tellurium crystals. The two principle reflecting powers, R_1 and R_2, for plane polarized light falling normally on one of the hexagonal surfaces of the crystal and with the electric vector respectively parallel and perpendicular to the principal crystalline axis, vary in the visible spectrum from 0.28 to 0.34 for R_1, and from 0.22 to 0.32 for R_2. These values agree very closely with those determined by Van Dyke (*J. O. S. A. and R. S. I.*, **6**, 917, 1922) who employed an indirect polarimetric method. (Compare abstract 29 above.)

45. A variable single band acoustic wave filter. G. W. STEWART, University of Iowa.—A single band filter previously reported upon, SB9, consists of a conducting tube with branches at equal intervals. Each branch consists of a volume with an orifice in parallel with a tube terminating in the surrounding atmosphere. By slipping into the conducting tube a cylinder of paper with punched holes, the opening into the branch could be readily altered. The radii of the openings tested were 0.243 cm, 0.15 cm, and 0.05 cm. The lower limiting frequency remained unchanged with the variations in the orifice, whereas the upper limit was altered thereby. This is in strict accord with the requirements of the theory and supplies a striking confirmation of the correctness of the formulæ derived. The experimental upper limiting frequencies for the three cases, with the theoretical values in parentheses, are as follows: 455 (510), 390 (440), and 350 (385).

46. Crystal structures of some sulfides, selenides, and tellurides. MAURICE L. HUGGINS, Harvard University.—The electronic structures previously given for the atoms of Zn, Cd, Hg (divalent), Cu (monovalent), Ag, Au, S, Se, and Te (*J. Phys. Chem.*, **26**, 601, 1922) indicate that the arrangement of atoms in crystals of the sulfides, selenides, and tellurides of the electropositive atoms mentioned is probably one in which each metal atom is surrounded by four negative atoms at tetrahedron

corners, and each S, Se, or Te atom by four or eight electropositive atoms at tetrahedron or cube corners. This requirement for the Zn, Cd, and Hg compounds can only be met if they possess either the type of structure already found for the cubic form of ZnS or that found for the hexagonal crystals of ZnO, ZnS, and CdS, while the only possible structure fulfilling the above requirements for the Cu, Ag, and Au compounds is that possessed by CaF_2. The crystallographic data, in so far as available, are in complete accord with these structures. Very definite confirmation is obtained from a consideration of the interatomic distances, calculated from the densities on the provisional assumption that these structures are correct. The values for the radius of each metal atom calculated from the sulfide, selenide, and telluride agree within 0.01 A (except in the case of CdTe, where the calculated Cd radii are respectively 0.02 A and 0.03 A greater than those from CdS and CdSe). Furthermore, the Cu and Ag radii so obtained agree well with those computed from CuI and AgI, and the Cd value agrees with that obtained from the Cd-O distance in $CdCr_2O_4$. This suggests strongly that the assumed structures are correct. Density data are not available for Cu_2Te, Au_2S, Au_2Se, and Au_2Te. The last, however, forms isomorphous mixtures with Ag_2Te, hence it, at least, has the same structure. (Compare abstract 28 above.)

47. The settling of small particles in a fluid. MAX MASON and WARREN WEAVER, University of Wisconsin.—Small particles immersed in a liquid experience a motion which is the combination of a steady gravitational drift and a Brownian movement. If there are space variations in the density of distribution of particles, the Brownian movement produces a diffusion which tends to equalize the density. In the steady state the density n of particles is an exponential function of x, the distance below the surface of the liquid. This paper investigates the manner in which the steady state is established. A consideration of the combined effect of fall and diffusion leads to a partial differential equation for the number density of particles as a function of depth and time. A set of special solutions is obtained in terms of which a solution satisfying initial and boundary conditions can be expressed. (1) *Liquid of finite depth.* The solution is obtained for a liquid of finite depth with an arbitrary initial distribution $n_0 = f(x)$. For the case of uniform initial distribution a reduced form of the solution is obtained which contains a single parameter. This one parameter family of curves is plotted, and from these curves, either directly or by interpolation, may be obtained the density distribution at any time for a solution of any depth, density, and viscosity, and for particles of any size and density. For small values of t, since the solution obtained converges slowly, an image method is used to obtain an integral formula for the density. (2) *Liquid of semi-infinite or infinite depth.* In the case of a liquid of infinite depth the solution for an arbitrary initial distribution is expressed by the Fourier integral identity. The case of zero initial density for negative x, and constant initial density for positive x is calculated, as is also the case of particles initially uniformly distributed over a layer of depth h. In the case of a liquid extending from $x = 0$ to $x = \infty$, the boundary conditions are satisfied by assuming a suitable fictitious initial distribution over the range from $x = -\infty$ to $x = 0$. The cases of uniform initial distribution, and initial distribution over a layer, are calculated. The latter case, while derived for a liquid of semi-infinite depth, gives approximately the distribution of density during the settling of a layer of particles initially distributed uniformly over a depth h at the upper end of a very long column of liquid.

48. The spectrum of helium at very low pressures. R. T. DUFFORD, University of Chicago, and L. THOMPSON, Kalamazoo College.—By use of a double-cathode tube mounted in a weak magnetic field, sufficient light is obtained, without a capillary, for spectrum observations at pressures down to a few hundred thousandths of a milli-

meter. A small region between the cathode plates is subject to intense ionization as a result of the constraining action of the magnetic and electric fields upon the electrons (L. Thompson, PHYS. REV., **17**, 421, 1921). The following results were obtained with helium at pressures corresponding to a parallel spark gap of from 1 to 4 cm, using a small grating and a quartz spectrograph. (1) The brightest lines at these pressures belong to the helium and parhelium principal series. (2) The next brightest lines belong to the helium and parhelium first subordinate series, with the helium lines brighter than the parhelium lines. (3) The helium second subordinate series is represented by only one faint line (λ 4713) and has no lines visible at the lower pressures. The parhelium second subordinate series is absent except for the very weak line λ 5048 on one plate at high pressure. (4) None of the enhanced lines of helium appear. (5) With a high vacuum but with the potential reduced by a 5-mm parallel gap, the usual white cylinder of light between the cathodes assumes the characteristic green color and gave with an eleven-hour exposure only three lines of the two principal series as important lines, together with a few members of the first subordinate series of helium (λ 5876 very weak). (6) An essential difference between these spectra and the spectra obtained at higher pressures is the very marked shift of energy toward the violet among the lines of any one series. The first lines of a series to appear are those of ordinal numbers three or four.

49. Precision measurement of the crystalline structure of calcium oxide, calcium sulfide, and calcium selenide. WHEELER P. DAVEY, General Electric Company.—Using the method previously described (PHYS. REV., **19**, 538, 1922), the following results were obtained:

	Diffraction pattern.	Lattice of ions.	d.
CaO.....	FCC	SC	$2.395 \pm .002$
CaS.....	SC	SC	$2.843 \pm .003$
CaSe.....	FCC	SC	$2.957 \pm .003$

where FCC means face-centered cube and SC means simple cube. The CaO used in getting the above data was made by burning metallic Ca in oxygen. The CaS used was made by burning metallic Ca with the proper weight of S in an evacuated glass tube. When an attempt was made to burn Ca with Se in an evacuated glass tube, the reaction occurred with explosive violence, shattering the tube, but a brown scale was found upon the inner surface of the glass fragments. This scale was CaSe. A sufficient amount was obtained for the purpose of the experiment. An indication of the *speed of crystallization* is given by the interesting fact that this scale, formed during the instant of the explosion, was sufficiently crystalline to give a diffraction pattern.

50. Precision measurement of the crystalline structure of barium and strontium selenides. MABEL K. SLATTERY, Vassar College.—X-ray photographs were taken, using the method previously described by W. P. Davey (PHYS. REV., **19**, 538, 1922). As a calibration, NaCl is photographed on each film with the substance to be analyzed. The value of each line is then allowed to contribute to the final value. BaSe was found to have a simple cubic structure of ions, with length of side of cube, $d = 3.308 \pm .003$ A. SrSe also crystallizes in a simple cubic lattice of ions with $d = 3.117 \pm .003$ A.

51. The photo-electrical properties of heated oxides. H. KAHLER, Yale University.—It was discovered by Case (PHYS. REV., **17**, 398, 1921) and verified by Merritt (PHYS. REV., **17**, 525, 1921) that the electronic emission from the glowing filaments of mixed oxides in radio vacuum tubes could be enormously increased by

irradiating the filaments with violet light. The object of this experiment was to see how pure CaO behaved under the same circumstances. A vacuum tube provided with a quartz window and with a filament of sublimed CaO on platinum was constructed. A high vacuum was maintained by a Langmuir pump and a good fore-pump. The heavy vapors were frozen out with a liquid air trap. After the filament had been incandescent for 30 minutes and was at the proper red glow, the thermionic deflection amounted to 20 cm with the scale at a meter's distance. Light from a quartz mercury lamp was allowed to fall upon the filament but there was no increase in deflection of over one half per cent. To test the effect of different parts of the spectrum, nine Wratten filters, selected so as to include the extreme portions of the spectrum, a water cell, a dilute solution of copper ammonium sulphate, and a thin hard rubber sheet which transmitted only the infra-red, were each calibrated for energy transmission and were used to filter the light from a 400-watt glass incandescent filament bulb, at a distance of 30 cm from the oxide filament, focused on it by means of a glass lens. It was found in every case that there was an increased electronic emission proportional to the energy falling on the filament and independent of the wave-length over the range 0.4 μ to 1 μ. The added deflections were sluggish and of the same general character as a thermionic phenomenon. It may be noted that in these experiments the effect of absorbed gas was probably largely eliminated through the intense preliminary heating. It seems evident that the experiments of Case and Merritt on mixed oxides have to do with a different phenomenon from that here studied, the former having the characteristics of a photo-electric emission, the latter of a thermionic emission. These experiments as well as those reported in the next abstract were performed at Cornell University.

52. The photo-electrical properties of the phosphors. H. KAHLER, Yale University.—The object of this experiment was to test the photo-electric properties of the Lenard and Klatt phosphor CaBiNa. This material is composed of calcium sulphide, calcium fluoride, sodium sulphate, a bismuth salt and small amounts of sulphur and calcium oxide, and various other high temperature reaction products. The experimental arrangement was similar to that used by Lenard and Saeland with Butman's modifications (*Am. Jour. Sci.*, **34**, 133, 1912).

Some samples several years old, six of the CaBiNa, one of the BaCuLiPo, and one of ZnS, were found to be still very active from a luminescent standpoint, but photo-electrically insensitive to light transmitted through a glass window. When a quartz window was put on the tube in place of the glass, however, there was an emission for light from the quartz mercury lamp, three times as great as the emission from the same area of a freshly scraped surface of lead. When these aged phosphors were exposed to an x-ray beam there was little appreciable electronic emission, although the intensity of the beam was sufficient to produce vivid luminescence of a calcium tungstate screen at one meter. Also the luminescence of the material under the action of x-rays was not over 1/100 that of the tungstate screen. Fresh phosphors, prepared by D. T. Wilber, using the method described by Lenard and Klatt, showed phosphorescence of the order of one tenth as much as old Lenard and Klatt CaBiNa specimens under the exciting action of a glass incandescent lamp. Unlike the old preparations these samples were photo-electrically sensitive to light that had passed through the glass window of the vacuum tube.

It seems that these facts as well as the facts brought out by Lenard and Saeland can be explained on the assumption that the luminescence and photo-electric effects are caused by two different constituents of the phosphor instead of one compound as Lenard claimed. On this basis the photo-electrically sensitive material becomes changed through chemical action with age and its sensitivity destroyed or the long wave-length limit shifted to the violet, while the luminescent centers seem to remain

active for a greater length of time. Pauli's statement (*Ann. der Phys.*, 40, 677, 1913) concerning the slight difference of wave-lengths required to excite phosphorescence and the photo-electric effect would seem to favor this view. There seems then to be little conclusive evidence, so far as this type of experiment is concerned, that phosphorescence is an end product of the photo-electric effect.

53. Interference measurements on the spectrum of manganese. GEORGE S. MONK, University of Chicago.—*Pole-effect, pressure-shift,* and *wave-lengths* for the stronger lines of manganese *between* λ *4470 and* λ *6021* have been measured. As a source a carbon arc was used, with the lower positive pole bored out and filled with MnO_2. An appreciable pole-effect is obtained at the positive electrode, the displacements being toward the red end of the spectrum in all cases. For the determination of wave-lengths only a small portion of the center of a 12-mm, 5-ampere arc was used, and it is believed that pole-effect is entirely absent from these results. The wave-lengths of forty lines have been measured. As standards, neon lines and iron lines of group *a* were used, the strongest component of the green mercury line serving as an auxiliary standard.

54. Interference fringes in the rectangular interferometer. A. A. MICHELSON, University of Chicago.—The interferometer is made up of two plane parallel plates and two plane mirrors, placed at the corners of a rectangle, the mirrors and plates all being adjusted very accurately, parallel, and at forty-five degrees with the rectangular path of the pencil of light from a broad source of approximately monochromatic light (a Cooper Hewitt lamp). The fringes are viewed by a telescope. This arrangement is equivalent to an air plate of thickness t on which the light is incident at an angle of approximately 45°.

Let ϕ = inclination of surfaces of air plate; ψ = angle of intersection; t = thickness of plate at $i = 0$ and $\theta = 0$; $45° + i$ and ϕ = respectively the horizontal and vertical projections of angle of incidence; P = distance from the surface at which fringes appear for $t = 0$; x_1, y_1 = coördinates (parallel to surface) in "focal" plane. Then if $p = \sqrt{2}\,P\phi \sin\psi - t$; $q = P\phi \cos\psi$; $r = x_1 \sin\psi + y_1 \cos\psi$; Δ = difference in path; the expression for the position of the interference fringes will be (omitting small quantities of second order): $pi + q\theta = \sqrt{2}\,\Delta - r$. The isochromatic lines are straight, and inclined at an angle whose tangent is: $\tan\gamma = p/q$. If α and β are the horizontal and the vertical angular apertures of the cone of rays entering the telescope, the *visibility of the fringes* is expressed by: $V = (\sin kp\alpha/kp\alpha)(\sin kp\beta/kp\beta)$, where $k = 2\pi/\lambda$. It follows that V is fair only when $p\alpha$ and $q\beta$ are small; that is (for given apertures) when $P\phi \cos\psi = 0$; $\sqrt{2}\,P\phi \sin\psi = t$. Hence the fringes are distinct only when $\psi = 90°$ and at a distance $P = t/\sqrt{2}\,\phi$. If ψ is not 90° the fringes may be still readily visible if the aperture is small. The inclination is still $\tan\gamma = p/q$, and the breadth β is given by $2\lambda/\beta = [(\sqrt{2}\,P\phi \sin\psi - t)^2 + (P\phi \cos\psi)^2]^{\frac{1}{2}}$.